Kamm

The structure of the dihydro-β-naphthoic acids and the correlation of ionization and structure in unsaturated acids.

THE STRUCTURE OF THE DIHYDRO-β-NAPHTHOIC ACIDS AND THE CORRELATION OF IONIZATION AND STRUCTURE IN UNSATURATED ACIDS

BY

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THESIS

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

OLIVER KAMM

ENTITLED The Structure of the Dihydro-β-napthoic Acids and The Correlation of Ionization and Structure in Unsaturated Acids.

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Doctor of Philosophy

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I wish to express my gratitude to Professor C. G. Derick for his direction and kindly suggestions throughout the course of this investigation.

Oliver Kamm

Table of Contents

INTRODUCTION

This research is a part of the general investigation of the correlation of ionization and atomic linking structure which has been in progress in this laboratory during the past five years. The laboratory investigation of this general problem has been concerned chiefly with the study of the effect, from the standpoint of ionization constants, of the substitution of a given atom or group into the paraffin monocarboxylic acids. In this field the probability of a correlation between the position of the substituent and the ionization constant of the acid had been clearly demonstrated[1] from the existing data. No such correlation was, however, found to exist in the case of the unsaturated acids, for this class of compounds furnished the exceptions to the general rules. So striking are these contradictions that special theories, like those of Flursheim[2], have been advanced to explain them.

The character of the work has suggested a method of attack as follows: First, the preparation of unsaturated acids of known structure; second, the demonstration of structure of the

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1. Derick. J. Am. Chem. Soc. 33, 1167, 1181 (1911).
2. This theory is referred to and discussed later.

acids whose constitution is uncertain, by means of reliable chemical methods; and third, the measurement of the ionization constants of these unsaturated acids with sufficient accuracy to warrant the drawing of conclusions of a quantitative character.

From the data thus obtained, the following questions were to be asked: Is the place influence[1] of a double union, when in a given position with respect to the carboxyl group, a constant? When several double unions are present simultaneously, is the effect additive? If a correlation is found, can it be used to predict the structures of compounds of unknown constitutions?

The study of the correlation of ionization and structure should ultimately assist in the solution of such problems as valence, the arrangement of the atoms in space, the effect of one atom or group upon another atom or group of atoms, etc. Its most important immediate value, however, is the prediction of the structures of compounds of unknown constitution.

Towards the solving of this important problem of structure, many other physical methods besides the method of ionization have been applied.

Refractivity, dispersivity, magnetic rotation, optical rotatory power, absorption spectra, molecular volume, heats of combustion, etc. have all contributed to this problem. An

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1. This term is explained in the historical part of this paper.

important distinction should, however, be drawn between the application of ionization and the methods mentioned above. The logarithm of the ionization constant is a free energy function, i.e. a measure of the tendency of a reaction to take place.[1] Most of the other methods used in the study of the correlation of physical properties with structure are measured in terms the physical significance of which is unknown from a free energy standpoint. This has not always been admitted, in fact it was not until quite recently[2] that thermochemistry has been freed from the fallacious theorem advanced by Berthelot in 1867 which is as follows: "Every chemical change gives rise to the production of those substances which occasion the greatest development of heat." The ordinary calorimetric determination of the heat of combustion is a measure of the change in total energy and not in free energy, since it is not carried on isothermally and reversibly.

In spite of this most fundamental character of the logarithmic function of the ionization constant, most authors treating of the correlation of physical properties and structure have neglected it altogether.[3]

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1. This is discussed in the historical part of this paper.
2. Nernst. Transl. of Sixth German Edition, page 702.
3. See chapter on "Physical Properties and Structure" in Cohen, vol. II, "Organic Chemistry for Advanced Students" (1913); also chapter on "Physikalisch-chemische Einflusse" in Henrich, "Theorien der Organischen Chemie" (1912).

The present work has been carried on with the acids in the naphthalene series for in this group the speed of reaction is slow and consequently the intermediate reduction products are more readily isolated in a pure state. Dangers due to oxidation and rearrangement are also less liable to occur than in the benzoic acid series. Moreover, it has been considered advisable to test out the correlation of ionization and structure in acids that contain the unsaturation in a ring of carbon atoms, and thus to eliminate the complicating influence due to cis-trans isomerism produced by the double union in many of the open chain acids, a factor which appears to have been neglected by most investigators in this field.[1]

The results of this investigation will be presented under three main divisions:

I. The Structure of the Dihydro-β-naphthoic Acids.

II. The Electron Conception of Valence: A Laboratory Search for Electromers.

III. The Correlation of Ionization and Structure in Unsaturated Acids.

The historical treatment of each of these problems will be considered under the respective subdivisions, the general historical

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1. Wegscheider, however, realizes the dangers from stereoisomerism and hence deals only with saturated compounds. See Monatsh, 23, 289 (1902).

review which follows being concerned mainly with the development of the problem of ionization and structure. From the standpoint of clearness, it has seemed necessary to deal with the theoretical considerations under the three respective subdivisions. The conclusions will be summarized at the end of each section.

GENERAL HISTORICAL

In his classic work on the ionization constants of organic acids, Ostwald[1] had in mind, even in his first article, a correlation between ionization and structure. Not only did he realize that this constant was often more important than other physical properties (boiling point, melting point, etc.) but he suggests also that for the first time a method is possible for measurement of the spatial arrangement of the molecule--a possibility for determining molecular structure. To fully appreciate the master we must listen to his inspiring words[2] :

> "Das Ergebnis, dass ein und dasselbe atom je nach der 'Stelle', welches es in der Molekel einnimmt, ganz verschiedene Wirkungen ausübt, welche um so grösser sind, je unmittelbarer die Beziehung des Atoms zum Säurewasserstoffatom ist, führt zu dem allgemeinen Schluss, dass diese Wirkungen Funktionen der <u>räumlichen Entfernung</u> der fraglichen Atome sind. Damit is aber zum erstenmale ein Mittel gewonnen, räumliche Messungen am molekularen Gebäude vorzunehmen. Ich bin keinen Augenblick im Zewifel, dass es langer und mühsamer Arbeiten bedarf, bevor solche Messungen zu Ergebnissen führen werden, welche ein allseitig zureichendes Bild von der Gestalt der Molekeln geben werden. Aber dass dies Ziel erreichbar ist, scheint mir schon jetzt unzweif haft zu sein."

According to Ostwald, the ionization constant is a product, the factors of which are dependent upon the nature and

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1. Z. physik. Chem. 3, 170-197; 3, 241-288; 3, 269-422 (1889).
2. Ibid, page 415.

arrangement of the atoms in the molecule, and hence analogous changes in a given homologous series should change the constants in the same ratio. Ostwald's factor represents the ratio of the substituted to the unsubstituted acids. We may illustrate it by considering the paraffin acids and their chloro substitution products.

Table 1#

	Ka^{25^o}	Ka^{25^o} for α chloro- acid
Acetic Acid	1.86×10^{-5}	1.55×10^{-3}
Propionic Acid	1.45×10^{-5}	1.47×10^{-3}
Butyric Acid	1.56×10^{-5}	1.39×10^{-3}

In the above three examples, the Ostwald factors for the chlorine atom would be 83, 101 and 89 respectively. Wegscheider[1] uses the factors 86, 109 and 93 respectively. (Average = 90 if we give five weights to Ostwald's value for chloro-acetic acid). Such factors, Ostwald states, are not identical, since the analogous changes in the molecule are not exactly identical; for example, in chloro-acetic acid, the chlorine atom is linked to a carbon linked to two hydrogen atoms, while in chloro-propionic acid the chlorine atom is linked to a carbon which is united to one hydrogen atom and a methyl group. Moreover, when two substituents are present, their effect is not

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Scudder. "Conductivity and Ionization Constants of Organic Compounds". (1914).

1. Monatsch, 23, 292 (1902).

additive[1]; i.e. the second negative substituent influences the first and vice versa.

> "The deviations from the rule are produced by the nature of the substance, and serve to draw attention to the causes of these secondary effects."[2]

The work of Ostwald was continued by Bethmann[3], Bader[4], Wegscheider[5], Walker[6], and others[7]. Wegscheider has shown that the influence of a negative substituent in the mono-carboxy paraffin acids decreases as it is farther removed from the carboxyl group. He also considers the effect of substituents in the o-, m-, and p- positions in the benzene nucleus. His work will again be referred to below.

Fichter and Pfister[8] have investigated the open chain unsaturated acids and have shown that the constants for β-γ unsaturated acids are larger than those for the α-β isomers. They have also indicated that the double-union does not behave like a negative substituent, for in the latter case there is an uninterrupted decrease in ionization constant as the negative substituent

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1. Ostwald. Loc. cit. pp. 177, 192, 248, 251.
2. Ibid, pp. 416.
3. Z. physik. Chem. 5, 385-422 (1890).
4. Z. physik. Chem. 6, 311 (1890).
5. Monatsh. 23, 287, 599, 316, 357, 405 (1902); 26, 1231, 1265 (1905)
6. Z. physik. Chem. 49, 82 (1904); 51, 708 (1905); 57, 600 (1906). J. Chem. Soc. 65, 576 (1894).
7. See also Lichty, Ann. 319, 380 (1901); Holleman and deBruyn, Rec. trav. chim. 20, 360; Lunden "Affinitatsmessunger". Sammlung chem-tech. Vortrage, vol. 14 (1909).
8. Ann. 334, 201 (1904).

is removed farther from the carboxyl group. Michael[1] has suggested an explanation of this on the basis of his scale of combined influence. The views of Fichter and Pfister as well as those of Michael will be referred to again in section three of this thesis, at which place Flurscheim's[2] theory will also be considered.

Recently Derick[3] has sought to obtain a more accurate quantitative correlation of ionization and structure than that expressed by the Ostwald factor rule. The thermodynamic reasoning involved is as follows: The true measure of a reaction to take place is not the decrease in total energy, but is measured by the decrease in free energy. For the reaction of ionization, therefore, the second law of thermodynamics presents the expression

$A = RT \ln K$, in which

A is the free energy of ionization,

R is the gas constant,

T is the absolute temperature, and

K is the ionization constant.

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1. J. Am. Chem. Soc. 34, 855 (1912).
2. J. Chem. Soc. 95, 718 (1909).
3. J. Am. Chem. Soc. 33, 1152 (1911); 33, 1167 (1911); 33, 1181 (1911); 33, 74 (1912).

Since in the above expression R is a constant, it becomes evident that the free energy of ionization is a logarithmic function of K. For this reason, positivity and negativity of groups must be measured in terms of the logarithmic function[1] of Kb or Ka respectively. In this connection, it is of interest to note that Ostwald[2], in deriving the relation between the heat of dissociation of an acid and its ionization constant, pointed out the necessity of using a logarithmic function of the latter. The Ostwald Factor Law as used by Ostwald, Wegscheider, Lichty, etc., is not a logarithmic but an algebraic function of the ionization constant and consequently is not a true measure of the desired influence; it merely represents the "ratio of the influence of all the atoms in the molecule of the substituted acid to those in the molecule of the unsubstituted acid."

Derick suggests that the influence of the given substituted atom must be freed from the influence of the other atoms. This is accomplished by considering the free energy of ionization of an organic electrolyte as made up additively of the separate influences of each atom in the molecule. The method given for the calculation of the place influence of the chlorine atom in the α-chloro-butyric acid is as follows:

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1. Ibid 33, 1154 (1911).
2. Loc. cit. pages 416-417.

$$I_{\alpha Cl} = \frac{\text{log K for butyric acid}}{\text{log K for } \alpha \text{ chloro-butyric acid}} - 1$$

$$= \left(\frac{-4.807}{-2.857} - 1 \right) = 1.682 - 1 = \underline{.682}$$

The value .682 represents the place influence of the given chlorine atom freed from the influence of the other atoms in the molecule, and represents the combined direct and indirect[1] influences of the substituents with reference to the ionizing group. The correction for the hydrogen atom displaced need not be applied since the place influences calculated for unsaturated acids show that its place influence is small and thus may safely be neglected. Since this place influence is a free energy function, the factors for the α chlorine atom when substituted into various aliphatic acids should be identical in each case. The following table will show them to be fairly constant, whereas the Ostwald factors are not.

Table 2

Acid	Place Influence α Chlorine Atom	Ostwald Factor
Acetic	0.683	83
Propionic	0.708	101
Butyric	0.682	89

Constant values are also obtained for the place influences of the β-chlorine atom, the γ-chlorine atom, etc. In the same

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1. Van't Hoff. Ansichten uber organ. Chemie I, 284; II, 252.

$$= \frac{\text{[illegible]}}{\text{[illegible]}} - 1$$

$$= \frac{-[illegible]}{-[illegible]} - 1 = [illegible] - 1 = [illegible]$$

the value .[illegible] represents the phase difference of the stress relative phase [illegible] from the difference of the actual phase in the [illegible], and represents the maximum stress and maximum difference of the maximum stress relative to the [illegible] stress. The expression for the [illegible] phase displacement [illegible] by applied stress the phase difference calculation for [illegible] shows that the phase difference is small and [illegible] be neglected. Since this phase difference is a first order [illegible], the theories for the [illegible] and [illegible] vertical dispersion modes can be considered to [illegible] the following table will show that in the Gauss[illegible] [illegible] equal Poisson's ratio.

Table

Mode	Lame [illegible] [illegible]	[illegible]
[illegible]	.[illegible]	[illegible]
[illegible]	.[illegible]	[illegible]
[illegible]	.[illegible]	[illegible]

Numerical values are also obtained for the phase difference [illegible] the [illegible] stress, the [illegible] phase, etc. [illegible]

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1. [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible]

manner, the place influence of other atoms and even for groups of atoms may be calculated. Finally, by reversing the method used in deriving the place influence (above) we may use the latter in calculating ionization constants of negatively substituted acids of known structure, or if the structure (position of negative substituent) of the acid is not known, we may determine the latter if we know the ionization constant of the acid. The methods of calculation for both mono- and di- substituted acids have been illustrated[1].

The use of the logarithmic function of the ionization constant has, however, accomplished more than the above, since it was found that the "Scale of Combined Influence" is approximately in the ratio of thirds. Derick[2] states,

> "When the 'scale of combined influence' for a negative substituent upon a carboxyl group in position (1) is 2, 3, 4, 5, 6, 7, 8, 9, 10, etc., the position of the substituent may be predicted if the ionization constant of the substituted and unsubstituted acids together with that of any similar α-substituted paraffin monocarboxylic acid is known. For example, the 'scale of combined influence' for chlorine in the monobasic paraffin acids upon the carboxyl group in position (1) is found from the following data:

	Ka	Log K	Factor
3 α-Chlorobutyric acid, $C_2H_5CHClCO_2H$	1.39×10^{-3}	-2.857	0.6825
4 β-Chlorobutyric acid, $CH_3CHClCH_2CO_2H$	8.94×10^{-5}	-4.049	0.1873
5 γ-Chlorobutyric acid, $CH_2Cl(CH_2)_2CO_2H$	3.0×10^{-5}	-4.523	0.0627
6 δ-Chlorovalerianic acid, $CH_2Cl(CH_2)_3CO_2H$	2.04×10^{-5}	-4.690	0.0229

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1. Derick. Loc. cit. 33, 1183 (1911); 34, 74-82 (1912).
2. Loc. cit. 33, 1182 (1911).

From this it is evident that the scale for combined influence for chlorine in the monobasic paraffin acids upon the carboxyl groups in position (1) is:

$\alpha : \beta : \gamma : \delta$ (or 3 : 4: 5: 6) = 0.6825 : 0.1873 : 0.0627 : 0.0229

If we call the α-factor one we have:

$\alpha : \beta : \gamma : \delta$, etc., = 1: 1/3 : 1/9 : 1/27, etc.

In other words the effect of substituting chlorine in the β-position is about 1/3 of that in the α-position, similarly that of the γ-position 1/9 and that of the δ-position 1/27."

The advantages and disadvantages of the Derick "Place Influence" as compared to the Ostwald "Factor Rule" have been discussed in detail by Wegscheider[1]. Since the latter writer has questioned the theoretical derivation of the place influence factor, Derick and Hess[2] have recently derived a more strictly thermodynamic function. The new place influence is, however, not proportional to the first factor, since the value lnKn assumed to be a constant is really a variable. This derivation will be given here only briefly.

$$I = A = R\ T \ln K$$

where I is defined as the influence of all the atoms in the molecule upon the free energy of ionization. Let us represent this value by In for the negatively substituted acid and by Io for the unsubstituted acid, the corresponding ionization constants being represented as Kn and Ko respectively. The place influence of the substituent is therefore derived by

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1. Z. Electrochem. 18, 277-81 (1912).
2. M. S. thesis. Univ. of Illinois, 1914.

subtracting Io from In since the free energy of ionization is assumed to be made up additively. We obtain

$$In - Io = 2.302\ R\ T \log Kn - 2.302\ R\ T \log Ko$$

$$= 2.302\ R\ T(\log Kn - \log Ko)$$

which value is the place influence (I) of the substituent, and is to be used instead of the previously derived factor.

In comparing the Ostwald factor with the Derick place influence, Wegscheider has, however, neglected a very important argument in favor of the latter. In order to predict ionization constants according to the former method, we must know the Ostwald factors for each position (α, β, γ etc.) for no definite relationship is suggested between the respective ratios. According to the latter method, however, we may do the same thing if we know only the place factor for the alpha position, since we can predict those for the other positions by using the rule of thirds.

More recently still, Michael[1] has published a criticism of the ideas expressed by Derick. The former states[2]

> "It is open to question whether the use of values representing free energy of ionization, instead of those of ionization constants, is at present of much importance as what is now most urgent in this field is not a restatement of explanations in other terms, but a clearer insight into why so many facts elude a consistent theoretical treatment."

It is clear, however, to anyone who has read Derick's publi-

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1. J. Am. Chem. Soc. 34, 849-55 (1912).
2. Ibid. Footnote, page 855.

[illegible] to [illegible] the [illegible]

is assumed to be made on [illegible]. In which

$$\ln - \log = 2.302 \; [\log \ln - 2.302 \; [\log$$

$$= 2.302 \; [\log \ln - \log \; \ln]$$

which really is the place inflexion (i) of the [illegible],

is to be read instead of the previously derived [illegible].

In comparing the Lowell Mirror with the Mirror

place inflexion, [illegible] has, however, contributed a very

important argument in favor of the latter. In order to [illegible]

localizing mechanism according to the Turner method, we may

use the usual formula for each position (, ,) [illegible]

to [illegible] relatively is supposed between the regularity

points. According to the Turner method, however, we get an

even value if we use only the place factor for the right

position, since we can predict those for the other positions

using the rule of [illegible].

More recently Will, Lohmann[1] has published a criticism of the ideas expressed by Turner. In Turner's words[2]

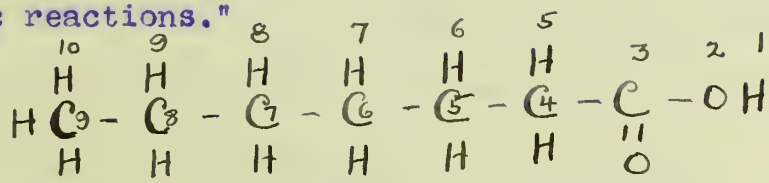
> "It is open to question whether the use of values [illegible] any first analogy of localization, instead of those of localization constants, is in presence of such [illegible] as that is the most [illegible] in this field is [illegible] achievement of explanations in other terms, but a [illegible] insight into why an [illegible] there exists a [illegible] [illegible] treatment."

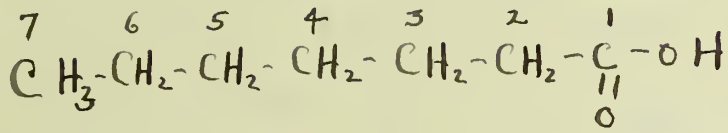
It is clear, however, to anyone who has read [illegible] [illegible]

1. [illegible], [illegible], [illegible].
2. [illegible], [illegible], [illegible].

cations that the object sought <u>is and has been</u> "a clearer insight into why so many facts elude a consistent theoretical treatment."

Michael and Derick differ fundamentally in the "order of the scale of combined influence." If we start with the carboxyl hydrogen in position 1, the scale of combined influence, according to Michael, is in the order 1-2-5-6-4-3-7-9-10-11-8, whereas according to Derick, the order should be 1-2-3-4-5-6-7-8-9-10-11, etc. The two orders are illustrated in the following examples, the first representing Michael's scale of influence which was presented only for atoms but for all reactions; the second illustration represents Derick's order of influence which was presented for both atoms and groups but only for the reaction of ionization in water solution under defined temperature and pressure. Michael is therefore not justified in saying that "it would fail utterly if it were applied to explain organic reactions."[1]





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1. Ibid, page 852.

Whichever system of nomenclature is used, the relative scale of influence of each author would be the same.

From the data available for the negatively substituted paraffin acids, we may say that the order of influence decreases as we go from the α to the δ carbon which is in agreement with both scales of influence. Because of the instability of the negatively substituted paraffin acids having the substituents in position 4 in Michael's scale, we must place the negative substituent (atom) into positions 8 and 9 respectively in order to test the application of the "Michael Scale" to the reaction of ionization. This has been done recently by Derick and his students.[1]

In conclusion, the foregoing will be discussed briefly. The "place influence" as first presented by Derick has pointed out the valuable "rule of thirds" which was accurate enough to be used for the prediction of ionization constants. In deriving the expression from a strictly thermodynamic basis, the rule of thirds is partly lost. If it is found (after obtaining more accurate conductance data) that the rule <u>does</u> hold, then a similar rule must hold in the case of the Ostwald Factor Law. Since the

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1. Not yet published.

new place influence[1] is the logarithm of the Ostwald Factor, then we will obtain the same rule by taking the cube roots of the Ostwald Factors. Moreover, there is no advantage in using the logarithm of the Ostwald Factor rather than the Factor itself, since both give the same results when used to calculate ionization constants. Also, if the Ostwald Factor is merely a ratio, and does not free the influence of a given atom from the influence of the other atoms, then it is difficult to see how the logarithm of this ratio has done this. The logarithmic function will find its justification, however, when a new variable (as seems to be necessary to explain the ionization constants of poly-substituted acids) is introduced.

Both the Ostwald Factor and the Derick "Place Influence" fail to explain satisfactorily the ionization constants of certain poly-substituted acids, the variation from the observed values being about 25 - 35%.[2] In the case of disubstituted aliphatic acids like dichloro-acetic acid[3], α,α-dibromo-propionic acid, etc., prediction is even less reliable if we use the factor obtained from the introduction of the first chlorine or bromine atom. Ostwald, therefore, determines the factor due to the introduction of the second substituent, by laboratory measurements and not by predictions, and finds its effect to be small

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1. Hess' Thesis, Loc. cit.
2. Wegscheider. Z Electrochem. 18, 277-81 (1912).
3. These acids would be expected to obey the mass-law only at higher dilutions.

one place following, is the location of the [illegible] [illegible] [illegible] will obtain the same rule by taking the same part of the [illegible] stimulus pattern. However, there is no advantage in using the logarithm of the stimuli rather than the [illegible] [illegible] both give the same results when used to calculate [illegible] [illegible] stimuli. Also, if the stimuli [illegible] [illegible] [illegible] [illegible] not from the influence of a given stimulus from the influence of [illegible] other stimuli, then it is difficult to see how the logarithm of this ratio has been [illegible]. The logarithmic function will [illegible] justification, however, when a [illegible] is seen to be necessary to explain the location constancy of poly-substituted acids in [illegible].

[illegible] the stimuli [illegible] and the [illegible] [illegible] [illegible] [illegible] fail to explain satisfactorily the location constancy of certain poly-substituted acids, the variation from the [illegible] values being about 20 - 30 %. In the case of disubstituted aliphatic acids like [illegible] acid, [illegible] acid, etc., prediction is even less reliable if we use the factor obtained from the introduction of the first substituent in [illegible] stimuli. Stimuli, therefore, determine the factor for the introduction of the second substituent, by [illegible] [illegible] and not to predictions, and fails its effect to be [illegible]

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1. [illegible], [illegible], op. cit.
2. [illegible]. [illegible], 12, [illegible] [illegible].
3. These acids would be expected to [illegible] the [illegible] [illegible] higher dilutions.

as compared with that of the first negative substitient.

Predicting[1] the corresponding ionization constants with the use of the expression

$$I\ s = \frac{\log K \text{ unsubstituted acid}}{\log K \text{ substituted acid}} - 1$$

we obtain the values:

Table 3

Acid	Calculated $K_a^{25^\circ}$	Observed $K_a^{25^\circ}$
Dichloro acetic acid	.0100	.0514
α,α-dibromopropionic	.00727	.033
α,β-dibromopropionic	.00233	.0067
α,β-dihydroxy propionic	.00020	.00020

These differences between the calculated and the observed values are certainly greater than would be expected from the fact that we are dealing with transition electrolytes which do not obey the mass-law accurately except in dilute solution.[2]

The effect of the substituent appears to be some function of the ionization constant of the acid into which it is substituted. In the monosubstituted paraffin acids, this effect is not very noticeable since the unsubstituted acids differ only slightly in ionization constants; in the case of disubstitution, however, the ionization constant of the monosubstituted acid must be considered also.

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1. For method used see J. Am. Chem. Soc. 34, 74-82 (1912).
2. Kendall. Nobelinstitut, Vol. 2, No. 38.

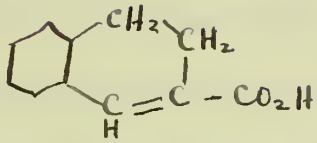
Part I

THE STRUCTURE OF THE DIHYDRO-β-NAPHTHOIC ACIDS

I.

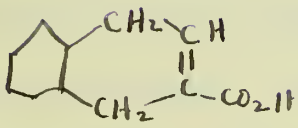
THE STRUCTURE OF THE DIHYDRO-β- NAPHTHOIC ACIDS

Three dihydronaphthoic acids which have an unsaturated linkage in the ring carrying the carboxyl group are theoretically possible, their structures being represented as follows:



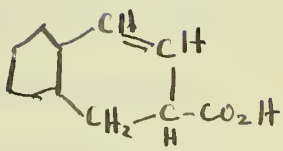
I

Δ^{1}-Dihydronaphthoic acid (2)#



II

Δ^{2}-Dihydronaphthoic acid (2)



III

Δ^{3}-Dihydronaphthoic Acid (2)

Of the above acids, two have previously been prepared and the structure of one of them has been definitely demonstrated. In the present work, which was carried out in connection with a study of the correlation of ionization and structure, the third isomeric acid has been prepared and demonstrations of the structures of the three isomers have been developed.

By the reduction of β-naphthoic acid with sodium amalgam, Sowinski[1] obtained two of the isomeric acids represented above. This work was repeated by Baeyer and Besem-

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The nomenclature used is that adopted by Meyer and Jacobson's "Lehrbuch der Organischen Chemie" (1903).

1. Ber. 24, 2354-2363 (1891).

felder[1] who obtained the acids in a higher state of purity. By reduction with sodium amalgam in the cold, a mixture consisting chiefly of the labile acid (so-called because of the ease of its rearrangement into the higher-melting stable isomer) was obtained, while reduction in hot solution yielded chiefly the stable acid. The mixture obtained in either case may be separated due to the different solubilities of the two isomers in water.

Structure III (above) has been assigned by Baeyer and Besemfelder to the labile acid not only because of the ease of its rearrangement into the stable isomer, but also because they found that with bromine it formed an unstable dibromide which decomposed spontaneously into a monobromolactone. This indicates that a bromine atom was initially present in the gamma position with respect to the carboxyl group which is possible only in the case of the dibromide derived from structure III. The same acid, because of the asymmetry of its molecule, should be capable of existing in two optically active components, and that such is the case has been shown by Pickard and Yates[2] who have prepared d-Δ^3-Dihydronaphthoic acid (2). This is a further confirmation of the structure of the labile acid since the two other isomers represent symmetrical structures.

The stable dihydro-acid obtained by rearrangement of the labile acid must therefore possess one of the two remaining

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1. Ann. 266, 187-202 (1891).
2. Soc. 95, 1011-1015 (1909); C. 1909 (2) 445.

structures (I or II above). Baeyer[1] as well as Meyer and Jacobson[2] from the data at hand have not attempted to differentiate between the two possible structures. Formula II has been suggested by Besemfelder[3] as the most probable structure because of the ease with which β-naphthoic acid is formed when the corresponding dibromide is digested with alcoholic potash. Under similar conditions, however, the monobromolactone derived from the labile dihydro-acid also yielded β-naphthoic acid. It is therefore evident that the behavior of its dibromide with alkali is an unsafe criterion for the assignment of the structure of the stable acid unless the dibromides of both the Δ^1 and Δ^2 dihydro-acids have been treated in this manner. This is now possible, for in the present work the third isomeric dihydro-acid has been prepared, The dibromide of the labile dihydro-acid has also been prepared and found to be fairly stable, not undergoing spontaneous decomposition as reported by Baeyer. It is therefore possible to study side by side the reactions of the dibromides of the three isomers. Thestructure of the new dihydro-acid has, however, been demonstrated independently by means of its oxidation products.

When the stable dihydro-acid (m. pt. 161°) is treated

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1. Ann. 266, 174 (1891).
2. Ibid.
3. Ann. 266, 198 (1891).

with water and an excess of barium hydroxide in a sealed tube at a temperature of 180°C., the third isomeric acid is formed. Its melting point after purification is found to be 118.5° (corr.). The same product may be obtained from the labile isomer, altho in some cases it is found contaminated with the 161° stable acid, indicating that the rearrangement has taken place with the formation of the latter as an intermediate product.

We might suggest the structure I as that of the new acid on the basis of this rearrangement, since we would expect the acid having the unsaturated union in intimate relation to both the carboxyl group and to the phenyl ring to be the most stable toward rearrangement. This has already been stated by Baeyer, who has also suggested the possibility of preparing the third isomer by a method analogous to the one used.

The method of preparation of the 118° acid (Δ^1) suggests that the same object might be accomplished by means of a strenuous treatment with concentrated potassium hydroxide solution at ordinary pressures and such was actually found to be the case. When either the labile or the Δ^2 stable acid is boiled with a solution of potassium hydroxide (1:2) for about eight hours, a 75% yield of the third isomer is obtained. It is separated from any unchanged acid and from the small amount of β-naphthoic acid formed by oxidation by means of fractional precipitation.

The 118° acid is analogous to the other stable acid

(Δ^2) and to Δ^1 unsaturated acids in general in its behavior. It is attacked instantaneously by potassium permanganate and with an excess is destroyed. In the cold, it adds bromine slowly. It was characterized by means of its dibromide and its amide as well as by analysis and a determination of its neutral equivalent. Additional tests of its homogeneity as a pure chemical individual are discussed in the experimental part of this paper.

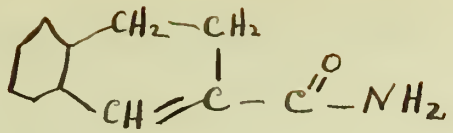
The melting points of the amides are as follows:

Table 4

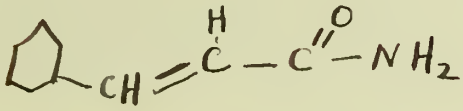
Acid	M. pt.	M. pt. of amide
Beta-naphthoic	184°	195°
Tetrahydro-naphthoic	96°	137°
Labile dihydro-naphthoic	101.2°	140°- 150°
Stable dihydro-naphthoic	118°	155°
Stable dihydro-naphthoic	161°	168°
Cinnamic	133°	148° #

The amide of the Δ^3 acid is of indefinite melting point because of a partial rearrangement into the stable Δ^2 acid during the preparation. The amides of both the Δ^1 and Δ^2 acids possess a strong cinnamon-like odor. The amide~~s~~ of cinnamic acid ~~were~~ was prepared and found to possess an identical odor. The analogy in structure is apparent.

The melting point of the amide of cinnamic acid is stated here because of the widely varying values (141.5° and 147°) found in the literature.



Amide of the 118° acid



Amide of cinnamic acid

As already mentioned, Baeyer and Besemfelder were able to prepare the dibromide of only one dihydro-acid, the dibromide of the labile acid undergoing spontaneous decomposition with the evolution of hydrobromic acid. By using a somewhat different procedure, the dibromides of all three isomers may be prepared without meeting any of the difficulties encountered by previous investigators. The dihydronaphthoic acids are all very soluble in chloroform while their dibromo- derivatives are not. The method used was to dissolve the acid in chloroform and to add the calculated amount of bromine also dissolved in chloroform, keeping the mixture cold. Under these conditions, the dibromo-derivatives separate out in the form of white crystals.

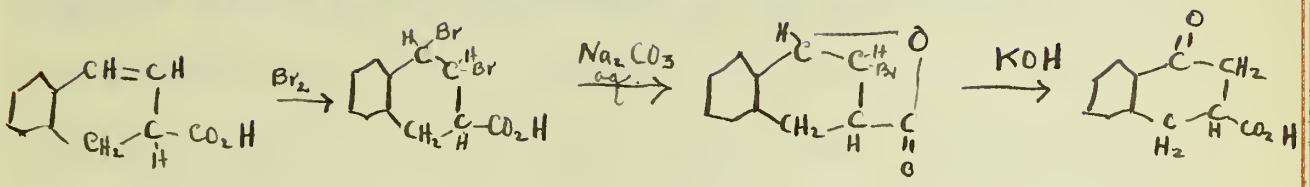
The melting points of the dibromides are as follows:

Table 5

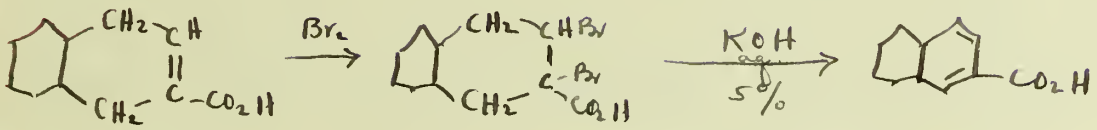
Acid	M. pt.	M. pt. of dibromide
Labile Δ^3	101.2°	172° with decomp.
Stable Δ^1	118°	190° " "
Stable Δ^2	161°	210° " "

Behavior of the Dibromides with alkalis. The three dibromides react in so characteristic a manner with dilute alkalis

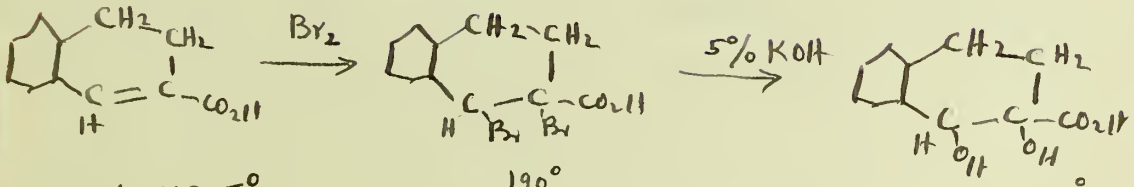
that this behavior may be used as a demonstration of the structure of the dibromides themselves and therefore of the corresponding unsaturated acids. In these decompositions, it is unnecessary to use boiling alcoholic potash, in fact the best results are usually obtained with a ten percent solution of sodium carbonate in the cold. The reactions observed are as follows:



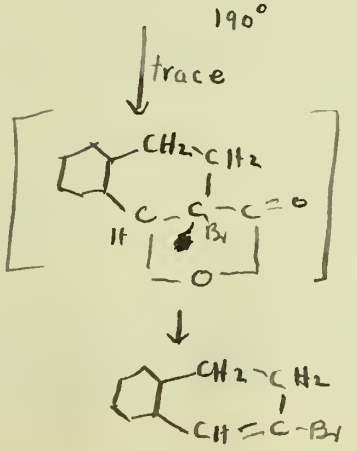
m. pt. 101.2° 172° 126.5° 143-45°

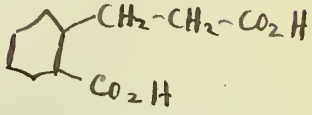


m.pt. 161° 210° 185.5°



m. pt. 118.5° 190° 182°





165°

The dibromide of the labile dihydro-acid when treated with sodium carbonate solution at first dissolves completely. Soon, however, a turbidity is observed and after a few minutes the monobromo-lactone separates. The dibromide of the stable (Δ^2) isomer dissolves readily in dilute alkali to a clear solution but is decomposed rapidly and almost quantitatively into β-naphthoic acid. This decomposition takes place even at a temperature of 0° (altho more slowly), no color changes being apparent. The dibromide of the 118° acid (Δ^1), on the other hand, undergoes the characteristic reactions observed when an α,β dibromo- acid is treated with alkali. If the solution is warmed, a deep blue color develops slowly, but finally disappears, a yellow solution remaining. At the same time a trace of an indifferent substance separates, due probably to the decomposition of an unstable β-lactone.[1] No trace of β-naphthoic acid was formed, the main product being the dihydro$\alpha\gamma$-acid represented above. Its formation is analogous to the decomposition of α,β dibromohexahydrobenzoic acid observed by Aschan[2]. Independent evidence of the structure of this dihydroxy- derivative and therefore of the dihydro-Δ^1 acid itself is offered by the oxidation of the dihydro$\alpha\gamma$-acid to o-carboxy-hydrocinnamic acid of known structure.

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1. The reactions of dibromocinnamic acid may be taken as an example. See Fittig, Kast, Ann. 206, 33; Nef, Ann. 308, 267.
2. Ann. 271, 281 (1893).

The reactions of the dibromides outlined above demonstrate that the three dihydro- acids described are distinct chemical individuals. The results confirm the conclusions of Baeyer and Besemfelder in regard to the structure of the labile dihydronaphthoic acid (structure III). Moreover, since the structure of this acid is known, and since we have prepared the third isomeric acid and its dibromide and made a study of the decomposition products of the latter, we may now accept the reactions of the dibromide of the stable (161°) acid as conclusive evidence that structure II is correct, while structure I should be given to the new isomer (118° acid).

More recently it has been found[1] that the dibromides of the dihydro- α-naphthoic acids react in an exactly analogous manner to that observed in the β-naphthoic acid series. This evidence can be used on the one hand to demonstrate the structure of the corresponding dihydro- α-naphthoic acids, and on the other is additional evidence in favor of the use of the reactions of the dibromides for the demonstration of structure.

<u>Demonstration of Structure by Oxidation</u>. Altho the reactions of the dibromides present satisfactory evidence in favor of the structure of the corresponding dihydro- acids, it was considered advisable to demonstrate the structures in an entirely independent manner. The method chosen was that of oxi-

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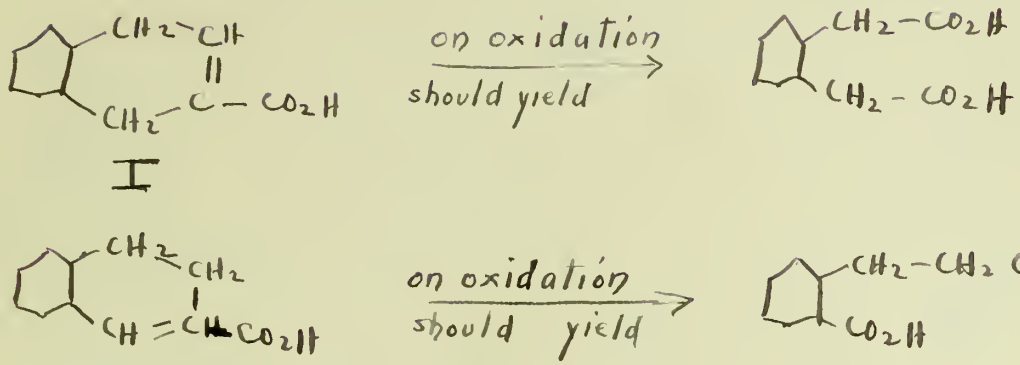
1. McCluggage, B.S. Thesis, Univ. of Illinois, 1915.

dation.

Meyer and Jacobson[1] state that the stable acid of Baeyer has either structure I or structure II below.



I

For this demonstration of structure by means of oxidation reactions, the new isomeric acid, Δ^1-dihydronaphthoic acid 2 was used, the oxidizing agent being alkaline potassium permanganate. Using this method, Baeyer and Shröder[2] had succeeded in demonstrating the s tructure of Δ^1-dihydronaphthoic acid 1, since upon oxidation o-carboxyhydrocinnamic acid was obtained. The β-isomer under examination should yield the same final product, and such was found to be the case. It was necessary, however, to apply very radical changes to the Baeyer method, since the first attempts always yielded products contaminated with large amounts of phthalic acid. The modified method adopted was to carry on the oxidation in steps, using the theoretical amounts of permanganate. The reaction observed

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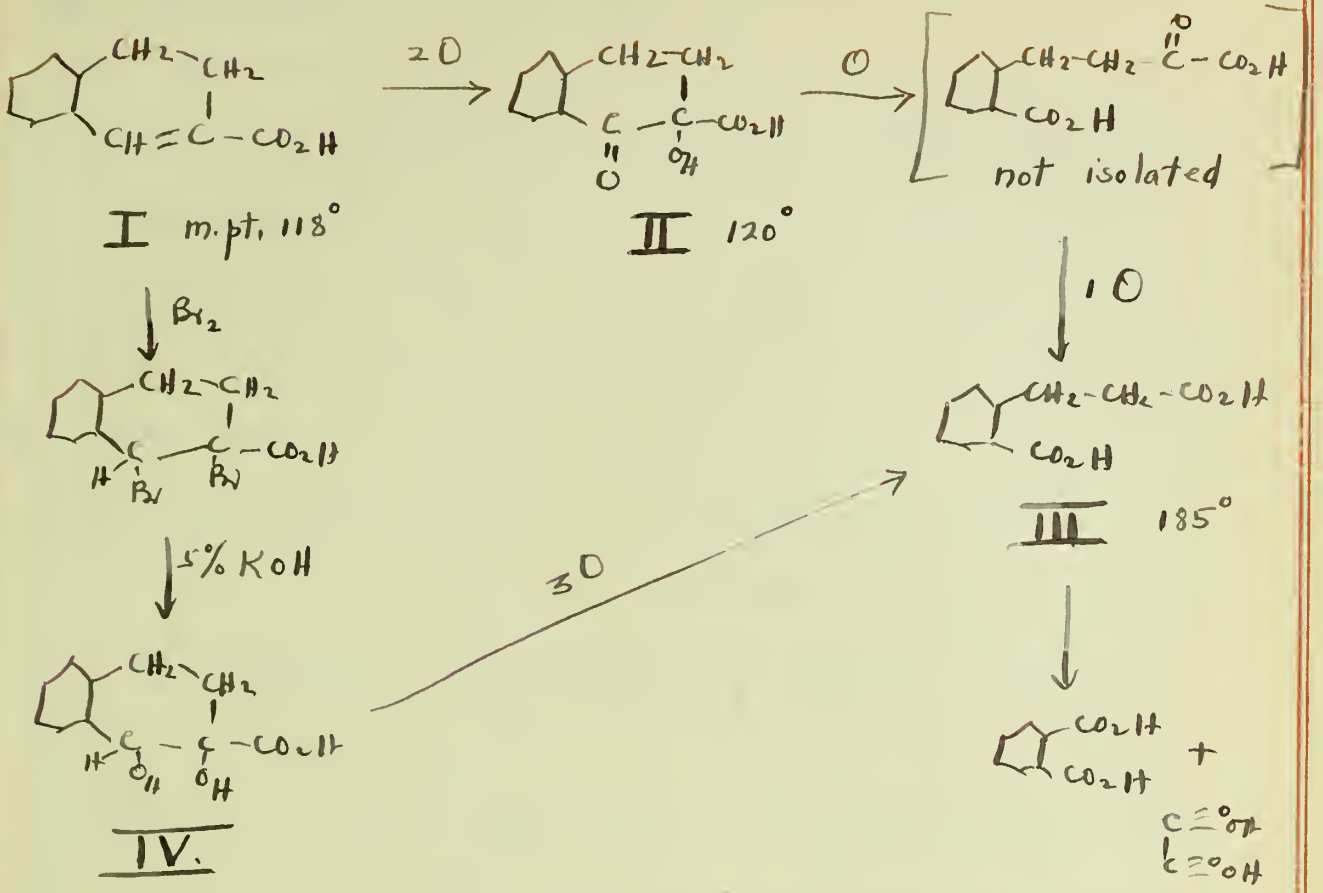
1. Loc. cit.
2. Ann. 266, 176 (1891).

was as follows:



The keto-hydroxy acid (II) was obtained in 50-60% yield, and from it pure o-carboxyhydrocinnamic acid (III) was obtained in 40% yield. The latter product was also obtained from the dihydroxy acid (IV).

Experimental Part

The Preparation of β-naphthoic Acid. This acid was prepared using the Sandmeyer reaction[1], starting with a pure grade of β-naphthyl amine. The nitrile was distilled with steam and hydrolysed as outlined below. This method yielded an exceptionally pure grade of β-naphthoic acid, which after one

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1. Gattermann. Fourth Edition (1903) Translated, page 221.

crystallization from dilute acetic acid melted at 185°. The yield was, however, less than 20% of the theoretical. For the preparation of large amounts of the acid, the following method is better adapted. β-naphthalene sulfonate was prepared as directed by Merz and Weith[1] except that the mixture of naphthalene and concentrated sulfuric acid was heated for six hours at 180°. The beta-sulfonic acid was separated as the calcium salt, recrystallized from water and then converted into the sodium salt. The yield of the latter was 625 grams from one kilo of naphthalene. The nitrile was prepared in the usual manner, by subjecting to dry distillation the sodium salt intimately mixed with an equal weight of potassium ferrocyanide. The yield of crude nitrile was 120 grams from 625 grams of sodium sulfonate, but can be improved by conducting the dry distillation under diminished pressure, or by distilling the mixture in small quantities. The yield of naphthoic acid from hydrolysis of 120 grams of nitrile was 100 grams. The method was materially improved in the following manner: In the dry distillation with potassium ferrocyanide, the yield is exceptionally poor if the calcium sulfonate is fused directly. If, however, potassium cyanide is used, the calcium salt itself may be substituted, without converting it into the more fusible sodium

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1. Ber. 3, 196. See also Ber. 20, 242.

salt. 40 grams of calcium sulfonate mixed with an equal weight of potassium cyanide and distilled in four portions yielded 18 grams of crude nitrile from which an almost equal weight of crude β-naphthoic acid was obtained.

The nitrile was hydrolysed as directed by Baeyer and Besemfelder[1], using a mixture of equal volumes of concentrated sulfuric acid, glacial acetic acid and water. The material insoluble in sodium carbonate solution should, however, not be discarded as directed but is boiled with 20% KOH solution, thus obtaining an additional yield of the acid which may amount to 50% of the total. A sample of the nitrile which had been purified by distillation was found to saponify more smoothly. It was in this case easily possible to stop the hydrolysis at the amide stage. The crude β-naphthoic acid was precipitated as the barium salt from a dilute hot solution of its sodium salt by means of barium chloride solution. The free acid was recovered by recrystallization from 30-50% acetic acid, bone-blacked, and purified by fractional crystallization. The pure acid melted# at 185.5°. Its amide (m. pt. 195°) was prepared

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1. Ann. 266, 187 (1891).

The melting points given in this paper refer to the capillary melting points, corrected for stem exposure. The corrections were almost negligible since calibrated Anschutz thermometers were used.

using one mole phosphorus pentachloride and decomposing the acyl halide with ammonia water. It was also obtained (m. pt. 194°) in the hydrolysis of the nitrile as mentioned above.

The Reduction of β-Naphthoic Acid. The reduction with three percent sodium amalgam in the cold, a stream of CO_2 being passed into the solution in order to neutralize the free alkali, yielded a mixture consisting of 75% labile dihydro and about 25% stable dihydro acids. Reduction in hot solution yielded the same two acids except in different proportions, 40% and 60% respectively. The labile isomer obtained by reduction in hot solution, however, contains appreciable amounts of the tetrahydro- acid#, from which it is separated only with difficulty. The methods of reduction and the use of fractional precipitation as described by Baeyer and Besemfelder have been found satisfactory. The advantages of the method of fractional precipitation over that of fractional crystallization for the separation of mixtures of isomeric acids should be further emphasized. The most soluble isomer is usually also the one having the largest ionization constant, and consequently the separation is unusually effective. The use of too concentrated solutions should, however, be avoided since this will result in the occlusion of the salt by the precipitated acid. The melting points of the acids have either been found to be as reported by

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Difficulties encountered due to the presence of this impurity are mentioned in Part II of this thesis.

Baeyer or slightly higher. Only in the case of the labile isomer was a lower value observed than that reported previously. Since the acid was to be used for conductivity measurements, it became necessary to investigate this point carefully. The melting point found was 101.2°, whereas the reported value is 104°.

Preparation of the Labile Dihydro-β-naphthoic Acid and the Separation of Isomers by Means of Fractional Precipitation. A typical reduction will be described here. Ten grams of pure β-naphthoic acid were dissolved in a small amount of dilute potassium hydroxide solution and the solution diluted to 100 cc. The latter was then cooled to 0° - 5°, a steady stream of carbon dioxide passed into it and 150 grams of crushed 3% sodium amalgam added at one time. Small portions (½ cc.) of the solution were withdrawn at ten minute intervals and tested with potassium permanganate.# The reduction was complete in forty minutes. The sodium carbonate solution is separated from the mercury, a few pieces of ice added, and the free dihydro-acids precipitated with hydrochloric acid. The precipitate, which consists of white crystals, is dissolved in very dilute potassium hydroxide solution (100-150 cc.) and the dihydro acids precipitated in fractions, using approximately normal

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The dihydro- acids are oxidized under these conditions while β-naphthoic acid is not. The permanganate is added until a permanent color is obtained, a small amount of sodium sulfite added and the solution acidified. If the reduction is incomplete the sparingly soluble naphthoic acid will separate.

hydrochloric acid, adding the latter slowly with a pipette. The ten fractions obtained were almost equal in weight (approximately 1 gram each); the first three consisted of cream colored flakes, while the others were more granular (typical of the labile isomer) and were pure white.

No.	M. pt. before recrystallization	
1	155-57°	Stable dihydro- acid
2	154-56°	
3	152-54°	
4	103.5°	Mixture of labile and stable acids
5	101.5°	
6	101°	Recrystallized from 30% acetic acid, m.pt. 101.0° Labile isomer
7	100°	
8	100.5°	
9	100.5°	
10	100°	

Fractions 7 and 8 after recrystallization were again subjected to fractional precipitation.

Refractionation of Fractions 7 and 8

No.	M. pt.
1a	100.2°
2a	100.8°
3a	100.8°
4a	100.8°
5a	100.6°
6a	100.6°

Fraction 3a was recrystallized from dilute acetic acid. White needles, m. pt. 101.1° .

Refractionation of Fraction 4 (m. pt. 103.5°)

No.	M. pt.	
1b	155-56°	Stable isomer
2b	154-56°	Stable isomer
3b	140-150°	Stable isomer
4b	102-103°	Mixture
5b	101°	Labile isomer
6b	101°	Labile isomer
7b	101°	Labile isomer
8b	100.8°	Labile isomer

Refractionation of fractions 7 and 8 shows that they are not further purified by a second fractional precipitation. Fraction 4 falls intermediate between the fractions of the stable isomer (m. pt. 161°) and the lower melting labile isomer. The results of the refractionation of this one gram fraction illustrates the effectiveness of the method. Fraction 9 was completely destroyed with an excess of potassium permanganate in alkaline solution. Examination of this solution failed to show the presence of tetrahydronaphthoic acid.

Several grams of the dihydro- acid (101°) were then converted into the dibromide by the method outlined below. From the pure dibromide, the original dihydro- acid was recovered with zinc dust in acetic acid solution. The recovered acid crystallized from dilute acetic acid and melted at 101°. It was again subjected to fractional precipitation and again shown to be homogeneous. The maximum melting point was 101.2° and was not changed when the acid was recrystallized from low-boiling

ligroin.

Rearrangement of the Dihydro- β -naphthoic Acids

Rearrangement with Barium hydroxide at 160°. Two grams of the labile acid Δ^3-dihydronaphthoic acid-2 were heated with an excess of barium hydroxide# (10 grams + 40 cc.water) in a sealed tube at a temperature of 160° for about six hours. When the tube was opened, a distinct naphthalene-like odor was noticed, altho decomposition with the loss of carbon dioxide was only slight. The barium salt of an acid was isolated. It was recrystallized from water and the free acid recovered. The latter melted at 118° and appeared to be a pure compound since its melting point was unchanged on subsequent purification from various solvents.

0.1470 gm. required 11.00 cc. 0.0764 N KOH
Neut. equiv. = 175. Theory for a dihydro- acid = 174.

The results are different from those obtained by Baeyer[1], who prepared a stable isomer melting at 160° by boiling the above labile acid in potassium hydroxide solution under atmospheric pressure.

The first experiment was then repeated, the acid being purified not by recrystallization of its barium salt but by

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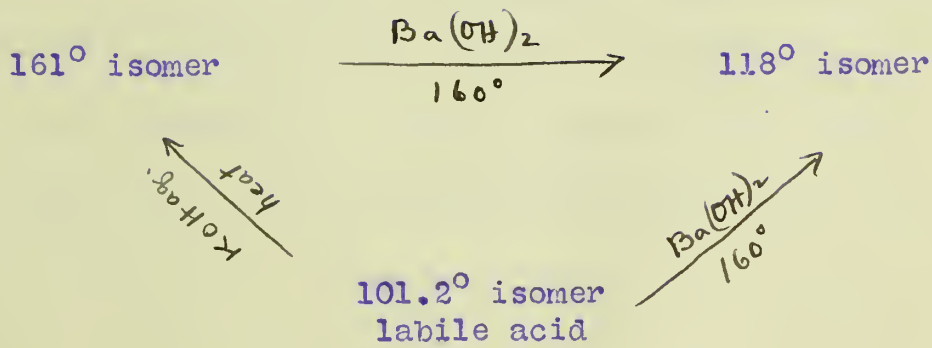
#. This procedure was initially used in an attempt to hydrolyse the compound at the double ~~isomer~~ union.

1. Ann. 266, 192 (1891).

means of fractional precipitation. It was found to be homogeneous since each fraction melted within the range of 115° - 117° and all melted at 118° after additional purification.

In a later experiment, however, Baeyer's stable acid (m. pt. 161°) was obtained in addition to the 118° product. It was found to be less soluble in water than the latter, and hence the two acids could readily be separated by means of fractional precipitation. The 161° acid is, however, obtained best by the direct reduction of β-naphthoic acid in hot solution, when it is obtained together with the labile isomer.

The stable acid (161°, now known to be Δ^2-dihydronaphthoic acid-2) was also treated with barium hydroxide under high pressure as had been the case with the labile isomer. Here also the new acid (m. pt. 118°) was obtained in addition to some unchanged product. The following diagram will represent the changes involved:



Both experiments were repeated using potassium hydroxide solution in place of barium hydroxide. The results were

identical with those already recorded. Variations in temperature and in the time of heating have also been used, but the results are similar to those given above and will not be repeated here.

Rearrangement Under Atmospheric Pressure. The rearrangement of the labile and stable acids using potassium hydroxide solution at atmospheric pressure was also investigated. Three grams of the labile isomer (m. pt. 101°) were boiled under a reflux condenser with 10% potassium hydroxide solution for about one hour. The mixture of acids obtained was separated by fractional precipitation and found to consist of almost equal quantities of the stable isomer (161°) and unchanged labile acid. The 118° isomer was not observed. This confirms the results reported by Baeyer and Besemfelder. It should be noted, however, that the amounts of β-naphthoic acid formed during this rearrangement due to the oxidation of the stable isomer by the oxygen of the air is almost negligible. Baeyer's statement[1] that the rearrangement is not a smooth one may be explained by the following experiments: Thirteen grams of the labile isomer (m. pt. 101°) which had been prepared and purified as described above were heated for four hours in a more concentrated potassium

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1. Loc. cit. page 192.

hydroxide solution than had been used in the previous experiment. (50 grams KOH dissolved in 100 cc. H_2O). Fractional precipitation yielded the fractions indicated below. It will be noted that the first four fractions consist chiefly of the stable isomer (161°) but appear to be less pure than the corresponding acid prepared by heating the labile isomer with more dilute potassium hydroxide solution. These low melting points are not due to admixture with β-naphthoic acid as Baeyer supposed, but are accounted for by the presence of the 118° isomer which is only slightly more soluble than the 161° isomer. Fractions 6 and 7 give evidences of the presence of the new isomer (118°) while the remaining fractions consist of unchanged labile acid. Fractions 1 to 7 were combined and again boiled with 1 : 2 KOH for four hours. In the same manner, fractions 8 to 13 were combined and boiled with 1 : 2 KOH for eight hours. The second column of melting points represents the fractions obtained after the second treatment with concentrated potassium hydroxide, while the third column gives the melting points of the fractions after recrystallization from acetic acid.

No.	M. pt.		No.	M. pt.	Recrystallized from 30% acetic acid
1	145-50°	Second KOH treatment	1a	114-15°	
2	145-50°		2a	114-15°	115.5°
3	145-47°		3a	114°	115.5°
4	140-45°		4a	114°	114.5°
5	124-27°		5a	114°	114.5°
6	117°		6a	101°	
7	116°				
8	100°	Second KOH treatment	1b	113-14°	
9	99°		2b	113-14°	115.5°
10	99°		3b	113-14°	115°
11	100°		4b	113-14°	115°
12	100°		5b	112°	115°
13	99°		6b	107-110°	112°
			7b	95-100°	110°

Fractions 2b to 5b were converted into the barium salt, the latter was recrystallized and the free acids recovered (m. pt. 116°).

These results show that both the labile and the stable isomers may be rearranged almost completely into the new isomeric acid (m. pt. 118°), the rearrangement of the labile isomer proceeding thru the intermediate so-called stable isomer (161°). It is apparent also that the new isomer is contaminated with a less soluble impurity from which it is not readily separated by means of fractional precipitation or by recrystallization.

Comparative conductivity measurements on the 116° acid obtained above and the purer 118° acid obtained by the barium hydroxide treatment, showed no difference between the two samples. The impurity present in the 116° sample must therefore be the

stable isomer (161°) which is less soluble, or extremely small amounts of the more highly ionized β-naphthoic acid. This problem was investigated quantitatively and it was found that the impurity corresponded to only two percent of the total weight of the 116° sample.

Purification of the 118° Isomer Thru the Dibromide. Five grams of the 115-116° sample were converted into the dibromide, using the method outlined below. From the dibromide, the dihydro- acid was recovered and found to melt at 118°. This recovered product was subjected to fractional precipitation and shown to be homogeneous. The maximum melting point of the 118° acid after recrystallizations from ligroin is 118.5°. The chloroform mother liquors from the preparation of the dibromide were allowed to evaporate spontaneously to one-half volume and a second small crop of dibromide recovered. The chloroform filtrate was extracted with dilute alkali to remove the last traces of the dibromides as well as any unchanged dihydro- acids together with naphthoic acid. From this alkaline extract, 0.10 gram of β-naphthoic acid was recovered. This might have been present in the 116° sample as such or it may have been formed from the action of alkali upon small amounts of the dibromide of the stable (161°) isomer. This separation of traces of 161° acid from the 118° isomer was repeated with known mixtures, and found satisfactory. These reactions are described in detail below, in

addition to other tests showing the 118° acid to be a pure chemical individual and not a eutectic mixture.

Δ^1-Dihydronaphthoic Acid-2 (118° isomer). The structure of this isomer is demonstrated below. A brief description of the acid together with some of the tests which have shown it to be a distinct chemical individual will be given here.

Analysis of 118° acid:

0.1798 gm. acid gave 0.4982 gm. CO_2 and 0.0923 gm. H_2O

	Required for $C_{11}H_{10}O_2$	Found
C	75.8%	75.6%
H	5.79%	5.75%

The analysis, the determination of the neutral equivalent given above, and the fact that the acid forms a dibromide, together with the analysis of the latter (below) proves that we are dealing with a dihydronaphthoic acid. To this we may add that the original acid, unchanged in melting point, is recovered from its dibromide as well as from its amide after purification of these derivatives. This would not be the case if we were dealing with a mixture. The 118° isomer is oxidized instantaneously by potassium permanganate in alkaline solution as is the case with other unsaturated acids. Five grams of the pure acid were dissolved in very dilute potassium hydroxide solution adding just enough alkali to dissolve the acid completely. The acid was then oxidized in the cold by the addition of ten grams of potassium permanganate

dissolved in 300 cc. water, the oxidizing agent being added slowly in the cold. After filtering off the MnO_2, the solution was evaporated on the water bath to a smaller bulk (50-100 cc.). Upon acidification of the clear, light yellow solution with mineral acid, no precipitate was obtained, showing the absence of both naphthoic acid and tetrahydronaphthoic acid. From the acidified solution, phthalic acid was obtained by ether extraction.

When a solution of several grams of the new isomer in chloroform was treated with bromine in chloroform, it was found that addition did not take place rapidly since even the first drop of bromine solution decolorized slowly. This is characteristic of stable acids in general, and is a definite proof that the labile acid (Δ^3-dihydronaphthoic acid-2) from which the new isomer had been prepared is absent, since the latter decolorizes bromine instantaneously. The reactions of the dibromides of the three isomers, however, gives even more conclusive proof than that above. The evidence from this source is presented in one of the following sections.

Finally, known mixtures of the 118° isomer with the 101° isomer, the 161° isomer and with β-naphthoic acid respectively, were prepared and it was found possible to secure separations by means of fractional precipitation.

The 118° isomer crystallizes from dilute acetic acid or from dilute alcohol in clusters of radiating needles. Its

degree of solubility in water, dilute acetic acid, ligroin, etc. is intermediate between that of the other two isomers. Preliminary measurements of the ionization constant of the 118° isomer have indicated that the value for this constant is very close to 3.0×10^{-5} at 25° in aqueous solution.

Solubility in Water of the 161° and 118° Isomers. The stable acid (161°) described by Sowinski[1] and later by Baeyer[1] is more stable toward melting point, solubility and ionization than is the new isomer described above. Toward rearrangement, however, the 118° acid is the most stable isomer under conditions discussed above. These measures of stability are not necessarily contradictory since they are determined under widely varying conditions. The solubilities of the two isomers in pure water at various temperatures were determined and it was found that the solubility curves do not intersect in the range examined. This solubility data is given in the following table. In order to make direct comparison possible, the results are expressed in terms of 10 cc. of the saturated solution. The amounts actually titrated were larger and at the lower temperatures amounted to 50 cc. The temperature coefficient of solubility for the two isomers is almost identical for the range 0° to 97°. This explains the difficulty found in separating these two acids.

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1. Loc. cit.

Table 6

Temp.	No. of cc. saturated solution	No. of cc. 0.0100 N $Ba(OH)_2$ solution used	
		118° isomer	161° isomer
96-97°	10.00 cc.	20.1 cc.	10.5 cc.
90°	10.00	14.6	8.0
80°	10.00	9.3	4.68
71-72°	10.00	6.7	3.48
55-56°	10.00	2.89	1.45
40°	10.00	1.34	.69
20°	10.00	.56	.34
0°	10.00	.39	.19

Preparation of the Amides. The amides of the three dihydro- acids and of the tetrahydro- acid were prepared as directed under the section dealing with β-naphthoic acid. To test out the method for unsaturated acids, the amide of cinnamic acid was prepared. The melting points have been given in Table 4, page 23.

Preparation of the Dibromides. The method used was similar to that recommended by Nef[1] for preparation of the dibromide of cinnamic acid. Three grams of the 118° isomer are dissolved in 10 cc. chloroform. To the clear colorless solution there are added slowly 3 grams of bromine dissolved in 5 cc. of chloroform, the solution being kept cold. (Besemfelder[2] used 100% excess bromine). The sparingly soluble dibromide begins to separate out after fifteen minutes. The mixture is, however,

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1. Ann. 308, 267.
2. Loc. cit. page 190 and 194.

allowed to remain in a dark place for two hours, after which only a faint bromine color remains; it is then filtered off using a suction filter and washed with 10 cc. chloroform. White crystals melting at 190°. Yield 5 grams. For the determination of the melting point and for the analysis, a product which had been precipitated from a more dilute chloroform solution was used.

0.1956 grams bromide gave 0.2219 grams AgBr

	Calculated for $C_{11}H_{10}O_2Br_2$	Found
Br	47.9%	48.2%

The dibromides of the labile (101°) acid and of the stable (161°) acid were prepared in an analogous manner; in each case the dibromides were found to be less soluble in chloroform than the corresponding acids and for this reason they may readily be obtained pure. Their melting points have been given in Table 5, page 24. No difficulty was found in preparing the dibromide of the labile acid since it did not decompose spontaneously as reported by Baeyer and Besemfelder.

0.2449 grams substance gave 0.2755 AgBr

	Calculated for $C_{11}H_{10}O_2Br_2$	Found
Br	47.9%	48.9%

<u>Reactions with Alkalis of the Three Isomeric Dibromides</u>. The dibromide of the labile acid (Δ^3-dihydronaphthoic acid-2) dissolves completely in 5% sodium carbonate solution. Soon, however, the clear solution becomes turbid and a precipi-

tate is formed which increases rapidly. The product formed was found to be the monobromolactone already described. One gram of the bromide yielded 0.6 grams (80%) of the lactone. M. pt. after recrystallization 126°. The fact that the initial product dissolves completely in dilute sodium carbonate, proves that the lactone is not present as a contamination of the bromide. When this lactone was boiled with 20% potassium hydroxide solution, it dissolved slowly and remained in solution after cooling. The following day, the solution was acidified, an insoluble acid being thrown down. M. pt. after one crystallization from water was 143-45°. Solubility in water = 1.5 gms. per liter. From the method of preparation, this product was suspected of being a keto- acid. This agrees with its neutral equivalent, its analyses and with the fact that it readily forms a semicarbazone. (M. pt. 266° decomp.). It is fairly stable toward the action of potassium permanganate in the cold.

.0977 gms. acid required 6.85 cc. KOH solution 0.0764 N.

Neutral equivalent = 187. Theoretical for keto acid = 190

.0772 gms. acid gave 0.1964 gms. CO_2 and 0.0367 gms. H_2O

	Required for $C_{11}H_{10}O_3$	Found
C	69.47%	69.36%
H	5.31%	5.29%

The dibromides of the 161° stable (Δ^2 dihydronaphthoic acid-2), when dissolved in 5% sodium carbonate solution or in 5% potassium hydroxide solution, decomposed smoothly with the loss of two molecules of hydrobromic acid into β-naphthoic acid. Boiling the bromide with alcoholic potassium hydroxide solution is unnecessary since the decomposition proceeds rapidly in aqueous solution even at 0°. From 0.4 grams of bromide, 0.19 gms. (90%) of pure β-naphthoic acid were obtained. This reaction agrees with that observed when Δ^2-dihydronaphthoic-1 is treated with alkali.

The bromide of the 118° isomer (Δ^1-dihydronaphthoic acid-2) was treated with cold 5% aqueous potassium hydroxide and the decomposition of the product followed by drawing off small portions of the solution at intervals. It was found that most of the bromide decomposed during the first minute, and that the reaction was complete in less than fifteen minutes. The color changes described in the theoretical part/take place on warming the solution but titration showed that no additional amount of alkali was required. The trace of indifferent substance already mentioned was separated by ether extraction from alkaline solution. It was a liquid possessing a fragrant odor and still contained bromine, Because of the small quantity formed in the reaction, it was not further examined altho the monobromolactone from the labile dibromide was shown to be absent.

The main product formed is a dihydroxy- acid. Because of the great solubility of the latter, it was separated from the acidified solution by repeated ether extractions. The fact that its solubility in ether is not great necessitates ten to fifteen extractions. It separates from the ether in white plates. From 3 gms. of the dibromide, 1.2 gms. (65%) of the dihydroxy acid was isolated. M. pt. 182°.

.0370 gm. acid required 6.15 cc. $Ba(OH)_2$ solution 0.0281 N.

Neutral equivalent found 214. Theory 208.

0.0780 gm. acid gave 0.1808 gm. CO_2 and 0.0415 gm. H_2O

	Theory for $C_{11}H_{12}O_4$	Found
C	63.46%	63.20%
H	5.82%	5.91%

The structure of this dihydroxy- acid is further demonstrated by the fact that under the conditions outlined below, it was oxidized to o-carboxyhydrocinnamic acid of known structure.

The reaction observed in the decomposition of the bromide of Δ^1-dihydronaphthoic acid-2 agrees with that of Δ^1-tetrahydrobenzoic acid and that of Δ^1-dihydronaphthoic acid -1.

Purity of the Dibromides. The reactions described above and also in the theoretical part of this paper may be used to test the purity of a given dibromide, in the following manner. The dibromide of Δ^3-dihydronaphthoic acid-2 is decomposed into the monobromolactone as described, and the latter separated by ether extraction. No acid is precipitated upon acidification of the alkaline solution. This shows that no trace of the dibromide of Δ^2-dihydronaphthoic acid-2 could have been present since the latter decomposes almost quantitatively under these conditions into the extremely insoluble β-naphthoic acid. Similarly, the dibromide of Δ^1-dihydronaphthoic -2 does not yield a trace of β-naphthoic acid. Neither could the monobromolactone of the Δ^3-isomer be detected. Hence the dibromide of the Δ^1-isomer must be free from the two other isomers.

Recovery of Dihydro- acids from the Bromides. The three dihydro- acids may be recovered from the corresponding bromides by treating the latter with zinc dust in glacial acetic acid. This method was found efficient as a means of purification and as a proof of the homogeneity of a given acid. This has already been described in detail in the section on the Preparation of the Labile Dihydro- β-naphthoic Acid, page 35.

Oxidation of Δ^1-dihydronaphthoic Acid-2. Proof of Structure. The method used by Besemfelder in attempting to isolate a definite oxidation product from the Δ^2-isomer was the addition of potassium permanganate in excess until a permanent color was obtained. Consequently a large excess of permanganate was used---17 gms. for 4 gms. of the dihydro- acid. In the present work, the following modification was adopted: The calculated amount of potassium permanganate was added slowly to the ice-cold solution of dihydro- acid dissolved in a very dilute alkali. In spite of these precautions, the only definite product isolated in several preliminary oxidations was o-phthalic acid or a mixture of acids consisting chiefly of the latter. The final method used was to carry on the oxidation in steps using about the theoretical amount (or 10% excess) of the oxidizing agent necessary to carry the oxidation to a given stage.

Five grams of Δ^1-dihydronaphthoic acid-2 (118° acid) are dissolved in 75 cc. water containing 3 grams KOH and the solution cooled with ice. For the oxidation, 6 grams of $KMnO_4$ dissolved in 500 cc. water are added slowly during a period of about one hour. Finally, the mixture is warmed on the water bath to coagulate the manganese dioxide. The latter is filtered off, using suction, and the filtrate evaporated down to about 100 cc. The yellow solution is then again filtered if necessary and acidified. After standing over night, the oxidation product

will have separated in the form of radiating clusters. An additional yield is obtained by ether extraction, bringing the total to 50-60% of theory. One recrystallization from water and treatment with bone-black yields a white product melting at 119-120°. In comparison with the dihydro- acid from which it is derived, it is very soluble in water.

.0462 grams acid required 10.50 cc. NaOH 0.0210 N

Neutral equivalent found 210.
0.1054 grams substance gave 0.2340 grams CO_2 and 0.0566 grams H_2O

	Required for $C_{11}H_{10}O_4$	Required for $C_{11}H_{10}O_4 + H_2O$	Found
C	64.04 %	58.9 %	60.5 %
H	4.90 %	5.40 %	5.98 %

This product is believed to be the keto- hydroxy acid or its hydrate indicated in the theoretical part of this paper. The titration value is not conclusive except that it shows that we are not dealing with the predicted dibasic keto-acid which would have a neutral equivalent of only 111. In a case of this kind, the titration is more conclusive than is the elementary analysis. The above product is suspected of being the keto- hydroxy acid with water of crystallization. The neutral equivalent of a sample soon after crystallization, having been dried on a clay plate for one hour, gave a value of 230. The initial product had been standing for several days. Several unsuccessful attempts were made to prepare a semicarbazone.

1.25 grams of the keto- hydroxy acid were oxidized to o-carboxy-hydrocinnamic acid by treating it with 1.3 grams of $KMnO_4$ under the conditions outlined above. In this oxidation, it is noticed that the permanganate is not decolorized as rapidly as in the oxidation of unsaturated acids. The dibasic acid is isolated as before except that it will separate from solution more readily than does the intermediate oxidation product. The product obtained is almost pure, melting at 164°. One recrystallization and treatment with a small quantity of bone black gives a 40% yield of a pure white crystalline product melting at 165.5°.

0.052 grams of acid required 24.8 cc. NaOH 0.0210 N.

Neutral equivalent found = 100. Theory 97

0.1424 grams of acid gave 0.3220 grams CO_2 and 0.0644 grams H_2O

	Required for $C_{10}H_{10}O_4$	Found
C	61.85%	61.67%
H	5.19%	5.03%

An attempt was made to oxidize the dihydroxy acid obtained from the dibromide of Δ^1-dihydronaphthoic acid-2 to the keto- hydroxy compound (m. pt. 119-120°). This was, however, not successful, altho some o-carboxyhydrocinnamic acid was

obtained, which serves to demonstrate the structure of the dihydroxy acid.

Conclusions

1. The missing isomeric dihydro-β-naphthoic acid has been prepared by rearrangement of both Δ^3-dihydronaphthoic acid-2 and Δ^2-dihydronaphthoic acid-2 and its identity as a pure chemical individual has been established.

2. The structures of the three isomeric dihydro acids have been demonstrated thru the reactions of the corresponding dibromides.

3. The structure of Δ^1-dihydronaphthoic acid has been conclusively established by means of oxidation reactions.

PART II

THE ELECTRON CONCEPTION OF VALENCE

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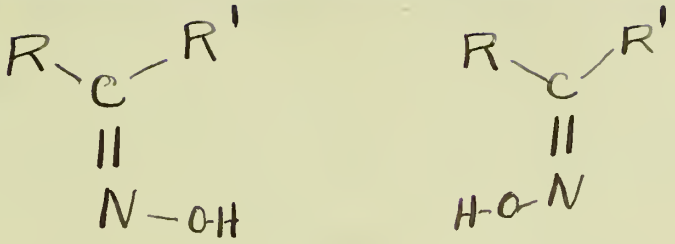
II

THE ELECTRON CONCEPTION OF VALENCE

A Laboratory Search for Electromers

According to the atomic linking theory as enlarged by LeBel and Van't Hoff, the following space formulae have been assigned by Hantzsch to the isomeric oximes of the type RR'C=NOH.



Certain advocates of the electron conception of valence, however, have sought to explain the entire phenomenon of geometrical isomerism upon a different basis. Falk and Nelson[1] make the following statement:

> "Without going into the advantages and disadvantages of 'geometrical isomerism', it may be pointed out that directive valences afford an explanation for the existence of isomers which does not involve the spatial relations between the groups at all but refers the isomerism to the double linkage between the atoms."

Accordingly, the following formulae, demanding an additional isomer, have been presented by them upon the basis of the electron

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1. Falk and Nelson. J. Am. Chem. Soc. 32, 1645 (1910). See also the Summary, Ibid, 32, 1653 (1910).

theory.

If the radicals R and R' were identical, no geometrical isomers would be predicted, whereas according to the electronic view, three isomers should be possible exactly as in the first case.

Even from the standpoint of the electron conception of valence, however, we must expect the possibility of space isomers. In the case of the double union $\underset{1}{C} \rightleftarrows \underset{2}{C}$ if carbon (1) sends an electron to carbon (2) and vice versa, each carbon atom loses one electron but also gains one electron with the result that there is no union between the two carbon atoms, unless we localize these charges. This view is not new but has been advanced previously.[1] The very theory which is put forth in an attempt to discard geometrical explanations thus actually demands the possibility of space isomerism. In the case of the oximes (above), at least six isomers might therefore be predicted, not

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1. This point was entirely disregarded in the first publication by Nelson and Falk. School Mines Quart. 30, 184-86 (1909). It was, however, added as a foot-note in their second publication. See foot-note, J. Am. Chem. Soc., 32, 1641 (1910). See also Lewis, J. Am. Chem. Soc. 35, 1452 (1913).

merely three, as represented by Falk and Nelson[1].

Not all adherents of the electron conception of valence have, however, followed Nelson and Falk in the applications of the theory to double-bond isomerism of the maleic-fumaric acid type. Even in cases where the theory has been of value in predicting the course of a reaction, the fundamental difference in the structure of the isomers has been explained upon a geometrical basis[2]. Some of the most active workers in organic chemistry still appear to consider isomers of the cis-trans acid type as differing in actual space arrangement, altho some may be willing to consider the possibility of electron isomers in addition to the ordinary cis-trans forms.

Falk and Nelson have applied the electronic explanation not only to the acids and oximes mentioned above but also to hydrazones, semicarbazones, ketones, etc., etc.. "All these classes may be referred to the direction of the two valences in the double bond without considering the spatial position of the groups. All double-bond isomerism may be attributed to the same cause."[3] This is mentioned as the most interesting result obtained in the application of the electron conception of valence[4].

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1. Additional complications might, of course, enter. See Fry's criticism, C.A. 1912, 2031, of Falk's paper, J. Am. Chem. Soc. 33, 1140 (1911) on the application of the electron conception of valence to organic acids.
2. See Stieglitz, J. Am. Chem. Soc. 34, 274 (1914).
3. J. Am. Chem. Soc. 32, 1650 (1910).
4. Ibid, 32, 1653 (1910) Summary.

of all authorities of the electron connection is well-known here, however, Poincaré, Abraham and Ritz on the application of the theory to double-fund interaction of the radio-frequency type. Yet in cases where the theory has been of value in guiding the course of a research, the fundamental difference in the structure of the lacunae has been neglected upon a (illegible) basis[1]. Some of the most serious warnings in connection (illegible) still appear to consider lacunae of the six-lines with type as differing in normal space arrangement, which does not be (illegible) to consider the possibility of electron lacunae in addition to the ordinary six-lines form.

Six and also have applied the electronic equipment not only in the works and values mentioned above but also to (illegible), (illegible), (illegible), etc., etc.. "If these changes may be referred to the direction of the two windows in the double fund without considering the spatial position of the groups. If double-fund lacunae are activated in the same change."[2] This is mentioned as the case interesting result in the application of the electron connection of values[3].

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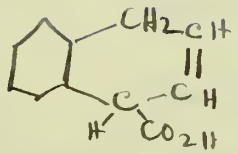
1. Additional negligible shift, of course, (illegible) (illegible). . 1911, i 21, of Ritz's paper. . . Phys. (illegible) 30, 124 '1911' on the application of the electron connection (illegible) values to (illegible) series.
2. Ve Triplite, . . Phys. Soc. 34, 274 '1911'.
3. . . Phys. Soc. 32, 190 '1911'.
4. (illegible) 32, 1921 '1911' (illegible).

The Method of Investigation

In the isolation of an electromer, we might expect most favorable results by working with a group of compounds in which the speed of reaction and hence of rearrangement is slow. This may be accomplished by choosing compounds of high molecular weight. In such cases, isomers are often found to be formed simultaneously. In the separation of keto-enol tautomers, similar methods have been used. Hantzsch was unable to isolate the two forms of nitro methane but the corresponding isomers in the case of phenyl nitro methane were easily obtained. The present work has been with compounds in the naphthalene series for in this group the possibility of isolating electromers is most alluring.

A second requirement in an investigation of this nature in which the isolation of isomeric compounds differing only in the arrangement of their electrons is sought, consists in excluding the possibilities of space isomerism. This has been done in the present investigation by choosing a class of compounds having the double union in a ring of carbon atoms, thus excluding the possibility of cis and trans forms due to the double union predicted by the theory of geometrical isomerism. For example, Δ^{2}-dihydronaphthoic acid -1

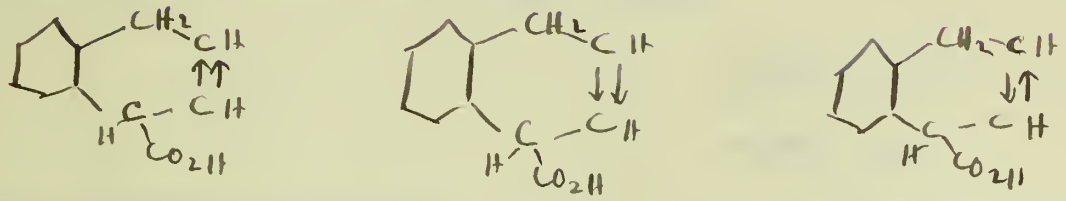


The Object of Investigation

In the isolation of an electrovalence, we might expect such favourable results by working with a group of compounds in which the effect of a-metals and bases of measurement is slow. This may be accomplished by choosing compounds of high molecular weight. In such cases, isomers are often found to be formed simultaneously. In the separation of vato-acid in isomers, analytical methods have been used. Attempts are made to indicate the form of ultra violets for the corresponding isomers in the case of phenol ether derivatives which usually vaporized. The present work has been with compounds in the naphthalene series for by this group the possibility of isolating electrovalence is more active.

Second requirement in an investigation of this nature is which can satisfactorily compounds different not in the arrangement of their electrons in space, consists in establishing the possibilities of space isomerism. This has been done in the present investigation by choosing a class of compounds having the bonds which in a group of carbon atoms, thus establishing the possibility of six and three forms due to the bonds which predicated by the theory of geometrical isomerism. Or stereo-

should not exist in cis-trans forms[1]. According to the electron conception of valence, the following three forms (at least) are predicted:



Similar possibilities for electronic isomerism would therefore exist in the case of the other dihydronaphthoic acids, five of which have been studied in the present investigation.

A third requirement in a search for electromers consists in the application of other methods of identification in addition to that of melting point, for the latter criterion would not distinguish between crystallin modifications and electromers. In the present research, conductivity measurements have been extensively employed.

In a third paper on the electron conception of valence, Falk[2] has applied the criterion of ionization constant to the organic acids and has suggested the following classification:

I.	$\rightrightarrows C - CO_2H$	ioniz. const. less than 0.01
II.	$\rightleftarrows C - CO_2H$	ioniz. const. 0.1 - 0.4
III.	$\leftrightarrows C - CO_2H$	ioniz. const. greater than 2
IV.	$\leftleftarrows C - CO_2H$	Too highly ionized to give satisfactory ioniz. constants

1. Optically active forms are of course possible and have been isolated.
2. Falk, J. Am. Chem. Soc. 33, 1140 (1911).

Similar possibilities for electronic transition solids therefore exist in the case of the other diamond-type solids, five of which have been studied in the present investigation.

Final requirement is a search for electronic anomalies in the application of other methods of identification in addition to that of melting point. For the latter criterion would not distinguish between crystallite modifications and electrotropes. In the present research, conductivity measurements have been extensively employed.

In a third paper on the electron compounds of valence, Alx^3 has applied the criterion of isomorphic substitution to the oxygen solids and has suggested the following classifications:

1. Ionic. Cross. Type . I
2. Ionic. Cross. . I - . 4
3. Ionic. Cross. Graphite Chan 3
4. do highly limited in type substitution

Ionic. Cross. Ionic. Cross.

Three kind of covers possible and have been indicated.

1. Ionic. . . Cross. Cos. Ox. Ox. Ox. Ox.

It is well known that the cis-trans forms of organic acids differ very greatly in ionization constants, in fact this has been used by Falk in assigning the following electronic structures to maleic and fumaric acids:

$CO_2H \cdot CH \rightleftarrows CH \cdot CO_2H$ fumaric acid

$CO_2H \cdot CH \rightleftarrows CH \cdot CO_2H$ maleic acid

The existence of more than two cinnamic acids has been used by Nelson and Falk as one of their strongest arguments in favor of electron formulae. Such electromers should, however, differ greatly in ionization constants for Falk indicates that the change in the direction of an electron will correspond approximately to a 1000% change in the ionization constant. The actual values are as follows[1]:

Table 7

	Ionization constant
42° isomer	$= 1.38 \times 10^{-4}$ at 25°
58° isomer	$= 1.41 \times 10^{-4}$ at 25°
68° isomer	$= 1.42 \times 10^{-4}$ at 25°

The three ionization constants do not differ by 1000% as predicted but are identical within the experimental error. It is evident that there is an argument against, rather than in

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1. The trans form (m. pt. 133°) has a smaller ionization constant (3.6×10^{-5} at 25°) as is general in all cis-trans forms. See also Ber. 46, 260. It might be suggested that the 42°, 58° and 68° isomers all change into the most stable electromer when in solution. Stobbe and Schonburg (Ann. 402, 187 (1913)) do not believe this to be the case since the respective acids could be recovered from solution. It seems strange that where the Van't Hoff theory predicts two space isomers, two so-called stable electromers may be obtained, whereas when only one form is predicted, only one of the many possible electromers happens to be a stable one.

It is well known that the ionization constant of acids differ very greatly in ionization constants, in fact this has been used to aid in assigning the following electronic structures to malic and fumaric acids.

The existence of more than two ionization acids has been used to claim such as one of steric arrangement in terms of electron functions. Such electronic shifts, however, differ greatly in ionization constants for acids indicates that the change in the direction of an electron will correspond approximately to a I^{-4} change in the ionization constant. The actual values are as follows[1]:

Table V

Ionization constants

60° lauric = $1.37 \times I^{-4}$ at 30°

60° lauric = $1.41 \times I^{-4}$ at 20°

60° lauric = $1.41 \times I^{-4}$ at 30°

The three ionization constants do not differ by I^{-4} as predicted but are identical within the experimental error.

It is evident that there is an argument against, however that in

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[1] The trans form (m. pt. 137°) has a second ionization constant $3.8 \times I^{-6}$ at 30° as is expected in all ole-trans forms. The di-cr. 80°, 30°. It might be suggested that the 60°, 10° and 20° isomers all change into the outer stable electronic state in solution and absorbing no. 4 2, 137° 137° do not believe this to be the case since the resonance energies would be considered first but-ning. It seems strange that where the '60°' 137° (trans) possesses the space isomers, the so-called stable electronic and in solution, whereas then only one form is predicted, only one of the two pos-sible electronic isomers happens to be a stable one.

favor or the electron conception of valence. Certainly the existence of the numerous cinnamic acids should not be used as evidence in favor of the electron conception of valence. Another argument based upon the existence of four cinnamic acids[1] has recently been advanced by Brunel[2] as a just argument against the theory.

Unfortunately the two benzophenones (See Schaum Ann. 300, 210-14) cannot be investigated from the same standpoint. They differ in melting point and in crystal form but possess the same boiling point, yield the same oxime, and the 26° isomer can be crystallized as the 48° isomer when its melt is innoculated

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1. The Theile partial valence theory demands the possibility of the existence of the isomeric cis-cinnamic acids, in which the partial valence on the oxygen of the carbonyl group would be represented as conjugated with the carbon atoms of the ring. See also Henrich, Theorien der Organischer Chemie, page 57.

Since, however, even the work of Stobbe and Schonburg (loc. cit.) leaves many points undecided, it will be best not to speculate further in regard to their structure at the present time.

2. Brunel. J. Am. Chem. Soc. 37, 709 (1915). "A Criticism of the Electron Conception of Valence." To answer Brunel's criticism, Falk and Nelson must, as Fry has pointed out, consider the direction of the electron joining the alpha carbon to the carbonyl group, thus accounting for six isomers. See Fry, J. Am. Chem. Soc.

Expanding upon this, we might predict according to the electron conception, twelve--twenty-four---or more, isomers according as occasion may require. The writer joins Brunel in exclaiming "There must surely be limits beyond which this attitude becomes unsafe."

level of the electron concentration, of course. Similarly, the existence of the numerous atomic units should not be used as evidence in favor of the electron conception of matter. Little arguement based upon the existence of their atomic units[1] has generally been advanced by "usual" as a just argument against theory.

Theoretically the two photoelectrons "on atoms in. g . ". -ie' cannot be investigated from the same standpoint. They differ in melting point and in arrested from not passed the same melting point, yield the same lozenge, and the 3d[2] layer, to be crystallized as the 4th layer when the melt is inoculated

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1. The Bohr partial valence theory demands the possibility of the existence of the isomeric oil-dimetric acids, in which the partial valence in the oxygen of the carboxyl group would be represented as conjugated with the carbon atoms of the ring. See also "Carbon", Thorpe and Whiteley's "Notes", page 37.

Once, however, even the many of "Lozenge and Chemistry" Inc. dit. Leaves many points undecided, it will be best not to speculate further in regard to their structure at the present time.

2. "usual". . . . "Ann. Ch. 37, 7 1 1 1 1 . " . " Principles of the Electron conception of physics." a summer "usual's principles, air and alkali salt, as by the pointed out, nonsalter the current lag of the electron yielding the alpha carbon in the carbonyl group, thus converting the air lamments. . . . . .

Speaking upon this, we might probably account for the stoichiometric valence, "Entre-tiq-Dom——on ment", (Lozenge according as nonsalt and positive. "A water joins usual in analysis. They just simply go into the carbon atom, the activity lozenge usual."

with a crystal of the latter. Moreover, the same investigators[1] who have indicated that the two benzophenones when melted are not identical, have shown that distinctions of this kind are lost in solution. Some caution should therefore be exercised in advancing their existence as evidence in favor of the electron conception of valence, since a theory should be based upon firmer grounds. The following example will emphasize this point:

May 9, 1914	Erlenmeyer[2] reports the preparation of optically active forms of benzaldehyde.
Aug. 4, 1914	Pauly[3] explains the discoveries of Erlenmeyer upon the basis of the electron conception of valence.
Nov. 17, 1914	Wedekind[4] proves Erlenmeyer to be wrong and shows conclusively that no optically active benzaldehyde was obtained.

Examples of the above nature suggest that more time might profitably be spent verifying data so as to base the theory upon firmer grounds.

Experimental Part and Discussion

The experimental part of the investigation of the reduction products of the naphthoic acids has been carried on during the past three years. In the course of this work, several hundred

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1. Schaum and Schaeling, Karl Schaeling, Inaug. Diss. Marburg, 1910.
2. Biochem. Z. 64, 382-92 (1914); 66, 509-11 (1914).
3. Biochem. Z. 67, 439-42 (1914).
4. Ber. 47, 3172-4 (1914).

[illegible] of the [illegible], [illegible], [illegible] [illegible]

who have indicated that the two decompositions from nuclear are not independent, have shown that discrepancies of this kind are [illegible] in solution. Some section should therefore be devoted to expounding their relations to evidence in favor of the electron exchange of neutrons, since a theory should be based upon [illegible] process. The following example will emphasize this point:

Jan 9, 1924 Flamberg[2] reports the preparation of optically active forms of benzidenhydr.

Feb. 4, 1924 Wolf[3] explains the discrepancies of Flamberg upon the basis of the electron exchange of neutrons.

Mar. 14, 1924 Staudinger[4] informs Flamberg to be wrong but shows conclusively that an optically active compound was obtained.

Examples of the above nature suggest that some kind might profitably be spent verifying data at as to make the [illegible] upon firmer grounds.

Experimental Work and Discussion

The experimental part of its investigation of the reaction products of the magnetic nuclei has been confined to the part, thus far. In the course of this work, several [illegible]

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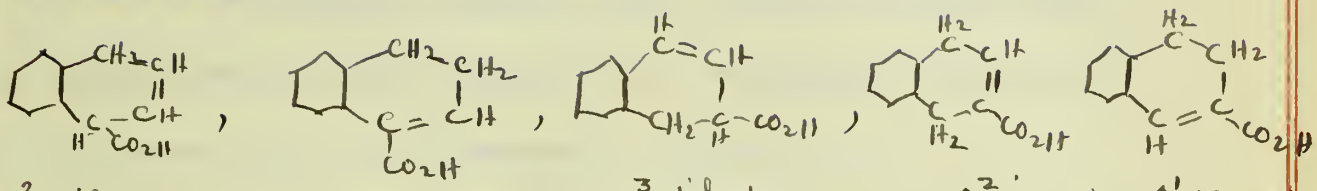
1. Gleason and Gleasing, Jnl. Chemistry, Chem. Ind. 1924, [illegible].
2. Ludwig, Ber. 56, 2[illegible]-2[illegible] 1924 ; 57, [illegible]-11 1924.
3. Ludwig, Ber. 57, 4[illegible]-4[illegible] 1924.
4. Ber. 57, 3[illegible]-4 1924.

separations of mixtures of reduced naphthoic acids, both in alpha and beta series have been carried out, primarily with the object of separating and purifying these acids since they were to be used in a study of the correlation of ionization and structure[1].

The following dihydronaphthoic acids have been used in this work:



Δ^2-dihydro-naphthoic acid 1 ; Δ^1 isomer; Δ^3-dihydro naphthoic acid 2 ; Δ^2 isomer ; Δ^1 isomer

Of the above acids, four have previously been prepared[2] but the structures of only two of them have been definitely demonstrated.[3] In the course of several investigations in this laboratory[4], the fifth isomer has been prepared and evidence has been obtained proving the structure of each of the five isomers.

According to the electron conception of valence as already discussed, each of the above isomers should, under proper conditions, be capable of existing in at least three forms. Consequently, in the preparation of the compounds and in their separation and purification, it might be hoped that a few of the

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1. Paper presented at the New Orleans Meeting, April, 1915. C.G. Derick and Oliver Kamm. "The Correlation of Ionization and Structure in Unsaturated Acids."
2. Sowinski. Ber. 24, 2354-63 (1891); Baeyer, Ann. 266, 187-202 (1891).
3. Meyer and Jacobson. "Lehrbuch."
4. Paper presented at the New Orleans Meeting, Oliver Kamm and C.G. Derick, "The Structure of Certain Hydronaphthoic Acids." "The Reduction Products of α-naphthoic Acid", McCluggage, B.S. Thesis, Univ. of Illinois, 1915.

and data matrix have been described and, primarily with the aspect of segmenting and partition these data which other users in the need in a study of the correlation of isolation and structure[1].

The following algorithmic points have been used in this work:

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1. Super processed as the on vision system, April, 1971.
Price and Hilvy Eds. The application of isolation and ... in medicated data.
2. Gallant, Mr. Sp. 2024-65 1971 ; author, ... Jan. 1...
3. Super and Jacobson. Unpublished.
4. Super processed at the ... on vision system, Hilvy ... Price, the structure of serial processing aids.
The adaption methods of ... , o ... India, Univ. of Illinois, 1972.

additional electromeric forms could be isolated. An attempt has also been made to isolate the intermediate products in the rearrangement of the labile dihydro- acids to the stable isomers. For this reason, the investigation was more exhaustive than it would otherwise have been.

In no case, however, were isomers obtained whose structure could not be explained by the atomic linking theory without the use of the electronic explanation.

The dihydro- acids represented above have been prepared by the following methods:

(a) The reduction of the naphthoic acids with sodium amalgam under varying conditions.

(b) By rearrangement of the labile to the stable isomers under widely varying conditions.

(c) From the dibromides by treating them with zinc dust.

(d) From the amides.

Since the procedure, as well as a part of the proof of structure has been given in the preceeding article, and additional information will be given in a subsequent paper, only a limited number of experiments will be given here to illustrate the method of attack.

Two grams of the labile acid Δ^{3}-dihydronaphthoic acid-2

[illegible]

[illegible] been made to explore the [illegible] problem of the re-
[illegible] of the Indian diagonal scale by [illegible] [illegible]
or [illegible]. The investigation was done extensively after it
[illegible] [illegible].

[illegible], however, some lessons original [illegible]
structure could not be explained by the simple [illegible] theory
[illegible] the use of the diagonal [illegible].

The [illegible] [illegible] structure have been pro-
posed by the following methods:

a. The addition of the [illegible] [illegible] will [illegible]
[illegible] under [illegible] conditions.

b. [illegible] rearrangement of the [illegible] so the [illegible] [illegible]
[illegible] under [illegible] [illegible] conditions.

c. [illegible] the difficulties by [illegible] [illegible] with [illegible]
[illegible].

d. [illegible] the [illegible].

Using the procedure, as well as a [illegible] of the [illegible] of
structure has been given in the previous article, [illegible]
information will be given in a [illegible] paper, only a limited
number of experiments will be given here to illustrate the [illegible]
of [illegible].

[illegible] of the Indian [illegible]

were heated with an excess of barium hydroxide# (10 grams + 40 cc. water) in a sealed tube at a temperature of 160° for about six hours. When the tube was opened, a distinct naphthalene-like odor was noticed, altho decomposition with the loss of carbon dioxide was only slight. The barium salt of an acid was isolated. It was recrystallized from water and the free acid recovered. The latter melted at 118° and appeared to be a pure compound since its melting point was unchanged on subsequent purification from various solvents.

0.1470 grams required 11.00 cc. 0.0764 N KOH

Neut. equiv. = 175. Theory for a dihydro- acid = 174

The results are different from those obtained by Baeyer[1] who prepared a stable isomer melting at 160° by boiling the above labile acid in potassium hydroxide solution under atmospheric pressure.

The first experiment was then repeated, the acid being purified not by recrystallization of its barium salt but by means of fractional precipitation. It was found to be homogeneous since each fraction melted within the range of 115°- 117°, and all melted at 118° after additional purification.

This procedure was initially used in an attempt to hydrolyse the compound at the double union.

1. Ann. 266, 192 (1891).

In a later experiment, however, Baeyer's stable acid (m. pt. 161°) was obtained in addition to the 118° product. It was found to be less soluble in water than the latter, and hence the two acids could readily be separated by means of fractional precipitation. The 161° acid is, however, obtained best by the direct reduction of β-naphthoic acid in hot solution, when it is obtained together with the labile isomer.

The stable acid (161°, now known to be Δ^2-dihydro-naphthoic acid-2) was also treated with barium hydroxide under high pressure as had been the case with the labile isomer. Here also the new acid (m. pt. 118°) was obtained in addition to some unchanged product.

Both experiments were repeated using potassium hydroxide solution in place of barium hydroxide. The results were identical with those already recorded. Variations in temperature and in the time of heating have also been used, but the results are similar to those given above and will not be repeated here.

An additional observation, which for a time was considered of unusual interest, will, however, be mentioned. Although as a general rule only the 161° and 118° isomers were obtained under the conditions outlined above when either the labile or stable isomers were subjected to the action of barium hydroxide under pressure, in a few cases what appeared to be a third isomer was isolated. Its melting point was found to be

[illegible] , however, [illegible] [illegible]

m. yr. 141[2] was obtained in addition to the 141[1] product. [illegible]

was found to be less soluble in water than the latter, and hence the two acids could readily be separated by means of fractional precipitation. The 141[2] acid is, however, obtained least in the direct production of -naphthoic acid in hot solution, when it is obtained together with the 141[1] isomer.

The acids made 141[2], now known as the -dihydro-naphthoic acid-2, are also obtained with various hydrocarbons under high pressures as well when the same with the 141[1] isomer. See also the work on m. yr. 11[2] was obtained in addition to some unchanged product.

The experiments were repeated using substituted naphthoic acids in place of benzoic hydrocarbons. The results were identical with those already recorded. Variations in temperatures and in the time of heating have also been used, but the results are similar to those given above and will not be repeated here.

A additional experiment, which for a time was thought of doubtful interest, still, however, be mentioned. Although as a general rule only the 141[2] and 11[2] isomers were obtained under the conditions mentioned above, either the 141[1] or 11[1] isomers were encountered in the action of benzoic hydrocarbons under pressure, in a few cases what appeared to be a third isomer was isolated. In melting point was found to be

90°. Only one example will be given. The products obtained by rearrangement of four grams of the labile Δ^3-dihydronaphthoic acid-2 were subjected to fractional precipitation. (The first nine fractions were almost equal in weight. Their color was either pure white or light cream.)

Fraction	M. pt.	M. pt. after recrystallization from 30% acetic acid
1	155-165°	117-118°
2	155-160°	117°
3	150-160°	117°
4	114-150°	115°
5	115°	114-115°
6	112-113°	114.5°
7	109-113°	113-114°
8	95-100°	106-111°
9	89°	
10	85-89° (ether extract from mother liquors)	

Attention was first directed to the unusual change in melting point of the first few fractions upon recrystallization from acetic acid. The cause for this is not the rearrangement of one isomer into another, but is due to the presence of a small amount of the ammonium salt of the acid[1] which is changed into the free acid upon crystallization from acetic acid solution.

The main product of the rearrangement in the last experiment evidently is the 118° isomer, altho the melting points indicate that the last few fractions are contaminated with other

---

1. The occlusion of the salt of the acid when the acid is precipitated from a solution of its ammonium salt is quite general, unless sufficiently dilute solutions are used.

[illegible] example will be seen. [illegible]

rearrangement of four atoms of the lactic [illegible]

acid-2 were subjected to thermolysis. The first

nine fractions were almost equal in weight. Their color was

yellow pure white or light green.

Fraction	gr.	gr. after recrystallization from 3 acetic acid
1	120-140°	114-116°
2	120-140°	116°
3	140-160°	117°
4	114-140°	116°
5	110°	114-116°
6	110-118°	114.5°
7	1 0-118°	112-116°
8	90-1 0°	1 0-111°
9	100°	
X	80-80°	water extract from mother liquors

Attention was first directed to the unusual change in melting point of the first few fractions upon recrystallization from acetic acid. The cause for this is not the rearrangement of one isomer into another, but is due to the presence of a small amount of the racemic salt of the acid[1] which is changed into the free acid upon crystallization from acetic acid solution.

The main product of the rearrangement in the last experiment evidently is the 116° isomer, with the melting point indicate that the last few fractions are contaminated with other

---

1. The resolution of the salt of one acid when the acid is separated from a solution of the racemic salt is quite complete, unless sufficiently dilute solutions are used.

substances. This had not been the case in the first few experiments recorded and in no case was it observed when the 161° isomer was subjected to rearrangement. Fractions 9 and 10 were again purified by fractional precipitation and yielded the product melting at 90°, the melting point of which did not change after several recrystallizations from dilute acetic.

0.2096 grams required 15.35 cc. 0.0764 N KOH

Neut. equivalent 178. Theory for dihydro- acid = 174

Tests of the purity of the 161°, the 118° and the 90° products. Each acid when dissolved in sodium carbonate solution and treated with potassium permanganate solution reacted instantly with the latter; i.e. test for unsaturation. When solutions of the respective acids in chloroform were treated with bromine in chloroform, it was found that addition of bromine took place slowly since even the first drop of bromine was decolorized slowly. This is characteristic of the stable acids and is a certain test that the labile acid (Δ^3-dihydronaphthoic acid-2) from which the three products had been prepared is absent.

The three acids form dibromides. The latter are best prepared by adding the calculated amount of bromine to the chloroform solution of the acid. The bromides are less soluble in this solvent than are the dihydro- acids themselves and will separate from solution in the form of fairly pure white crystals.

[illegible]

[illegible] was employed to remove impurities. Positions 2 and 3 were both purified by fractional precipitation and yielding the product melting at 2 °. The melting point of which did not change after several recrystallizations from dilute acetic.

2.94 grams required 10.38 cc. . The

[illegible] equivalent 177. Theory for dibromo- acid = 173

[illegible] of the purity of the 1a[illegible], the 1a[illegible] and the 2 [illegible] products. Each acid was dissolved in boiling methanol solution and treated with sufficient potassium carbonate solution [illegible] with the latter; i.e. test for neutrality. Then solutions [illegible] the respective acids in methanol were treated with barium [illegible] solutions. It was found that addition of barium ions [illegible] slowly since even the first drop of barium was precipitated slowly. This is characteristic of the crucic acids and is a certain test that the [illegible] acid [illegible] dibromohydroxybenzoic acid-2 from which the three products had been prepared is given.

The three acids form chlorides. The latter are [illegible] prepared by adding the calculated amount of thionyl to the chlorofoam solution of the acid. The benzoyl chlorides are less soluble in cold methanol than are the dibromo- acids themselves and will separate from solution in the form of fluffy white needles [illegible].

M. pt.	M. pt. bromide#
161°	172° with decomp.
118°	190° " "
90°	190° " "

The original acids may be recovered from the bromides of the 160° and 118° products upon treatment with zinc dust in acetic acid solution. The bromide of the 90° product, however, yields the 118° isomer when treated in this manner. Is this a rearrangement of one electromer into a more stable form? Is the 161° acid an electromeric modification of the 118° acid? Is it possible that we are dealing with the three electromers of Δ^2-dihydronaphthoic acid-2, the 118° and 161° acids being relatively stable, while the 90° product can be changed to the 118° acid through its bromide? The answers to these questions were as follows:

<u>Analyses of 118° and 90° acids.</u>

0.1798 grams of 118° acid gave 0.4982 grams CO_2 and 0.0923 grams H_2O

	Required for $C_{11}H_{10}O_2$	Found
C	75.8 %	75.6 %
H	5.79 %	5.75 %

0.1298 grams of 90° acid gave 0.3571 grams CO_2 and 0.0752 grams H_2O

0.2352 grams of 90° acid gave 0.6488 grams CO_2 and 0.1330 grams H_2O

The products have been shown to be dibromides by analyses, the results of which have been presented in a previous paper.

The original acids may be recovered from the brucines of the IA^{α} and IIA^{α} products upon treatment with alkaline dilute acid solution. The brucine of the β^{α} product, however, yields the IIA^{α} isomer when treated in this manner. This is reasonable since of one diastereomer into a more stable form. The IA^{α} acid has electrocyclic modification of the IIA^{α} acid. It is possible that we are dealing with the three diastereomers of -di-hydromyrtenic acid-3, the IA^{α} and IA^{β} acids being relatively stable, while the β^{α} product can be changed to the IIA^{α} acid through its brucinate. The measure of these properties were as follows:

Melters of IA^{α} and β^{α} acids.

.1741 grams of IA^{α} acid gave .4021 grams CO_2 and .1221 grams H_2O.

required for	found
$C_{11}H_{18}O_3$	
74.4 %	74.4
8.99 %	8.72

.1274 grams of β^{α} acid gave .2941 grams CO_2 and .1021 grams H_2O.

.1203 grams of β^{α} acid gave .2820 grams CO_2 and .1020 grams H_2O.

The products have been given to be diastereides of acetylene, the formula of which have been presented in a previous paper.

	Required for $C_{11}H_{10}O_2$	Found
C	75.8 %	75.1 %; 75.2 %
H	5.79 %	6.44 %; 6.34 %

Evidence obtained from conductivity measurements. In the first part of this paper, it was pointed out that conductivity measurements rather than melting points should be taken as evidence when identifying an ionizing electromer. Preliminary conductivity measurements[1] of solutions of the three acids gave the following results:

Table 8

	Ioniz. const. at 25°
118° isomer	3.0×10^{-5}
160° isomer	2.8×10^{-5}
90° isomer	$2.7 - 2.8 \times 10^{-5}$ (colorimetric)

From the consideration already presented, it is evident that we are here not dealing with electromers since the ionization constants differ by only a few percent, whereas electromers should differ by approximately 1000%, according to Falk.

Assignment of structure according to the atomic linking theory. The structures of the 161° and 118° isomers have been demonstrated both through the reactions of their dibromides as well as by oxidation methods. The results have already been presented on Part I of this thesis. The 161° isomer is Δ^2-dihydro-

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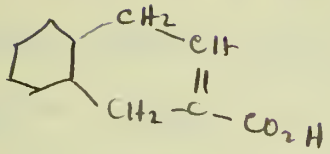
values obtained from conductivity measurements. In the first part of this paper, it was pointed out that conductivity measurements rather than melting points should be taken as evidence when identifying an ionizing electrolyte. Preliminary conductivity measurements[1] of solutions of the three acids gave the following results:

Table 1

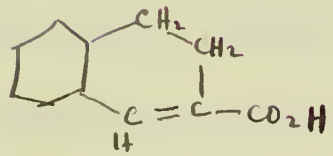
HIO^3 Iodic	3.4×10^{-4}	mole. cond. at 25°
$HClO^3$ Chloric	2.3×10^{-2}	
$HBrO^3$ Bromic	$2.7 - 3.7 \times 10^{-2}$	conductivity

From the consideration already presented, it is evident that we are here not dealing with electrolytes since the ionization constants differ by only a few powers, whereas electrolytes should differ by approximately 1 , according to the alignment of structures according to the Atomic Linking Theory. The structures of the HIO^3 and $HClO^3$ isomers have been designated both through their equations of state differentiation as well as by oxidation methods. The results have already been published in part of this thesis. The HIO^3 isomer is

naphthoic acid-2 (structure I below) while the 118° isomer is Δ^{1} dihydronaphthoic acid-2 (structure II).



I



II

The latter has been oxidized to o-carboxyhydrocinnamic acid, which was identified by its melting points, by its neutral equivalent and by analysis. It is further oxidized to phthalic and oxalic acids.

Oxidation methods have also solved the question concerning the 90° product. In spite of the fact that recrystallization and fractional precipitation did not change its melting point, it was found to be a mixture of ac-tetrahydronaphthoic acid-2 (m. pt. 96°) with the 118° acid. Upon oxidation, the pure tetrahydro- acid could be obtained. The source of the latter was found to be in one of the samples of the labile acid used in the rearrangements. This now explains why it was not obtained from the 161° isomer and explains also the somewhat high values for hydrogen and low values for carbon found in the analyses of the 90° "isomer." This recalls the fact that one of so-called "certain

[illegible] mole-% [illegible] [illegible] while the 111° isomer is [illegible] dichlorobenzyldiol mole-% structure [illegible].

[illegible] isomer has been validated to [illegible] which was identified by its melting points, by its neutral equivalent and by analysis. It is further validated to phthalic and benzilic acids.

Alkaline methods have also solved the question concerning the 9-° product. In light of the fact that [illegible] and theoretical precipitation did not change the melting point, it was found to be a mixture of [illegible] mole-% in. yr. 96°) with the 111° mole. Upon saponification, the pure [illegible] mole could be obtained. The source of the latter was found to be in one of the reactants of the benzile acid rearrangement. This was explained why it was not obtained from the 111° isomer but explains also the somewhat high values for hydrogen and low values for carbon found in the analyses of the 9-° isomer. This proves the last step was of an [illegible]

cases of isomerism" mentioned by Nelson and Falk[1] has since been shown to be based upon the melting point of a mixture.

The above will illustrate the method of attack which has been used in the present investigation. Because of the negative character of the work, however, the writer will only indicate briefly a part of it.

The reduction of β-naphthoic acid with sodium amalgam in the cold yielded a mixture of Δ^3-dihydronaphthoic acid-2 with Δ^2-dihydronaphthoic acid-2, but no other isomer could be separated. Reduction in hot solution yielded the same mixture except in different proportions, combined with a small amount of ac-tetrahydronaphthoic acid-2. Similar results were obtained when α-naphthoic acid was reduced in the same manner, the product being chiefly Δ^2-dihydronaphthoic acid-1 with only small amounts of Δ^1-dihydronaphthoic acid-1. The products of rearrangement under varying conditions of the Δ^2-isomer were carefully examined, not only in order to detect the possible occurrence of electromers, but also in an attempt to isolate at least traces of Δ^3-dihydronaphthoic acid-1. However, only the Δ^1-acid

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1. The Electron Conception of Valence. J. Am. Chem. Soc. 32, 1646 (1910). Gortner and Gortner, same Journal, 32, 1294 (1910). Hartley and Stuart, J. Chem. Soc. 105, 309-12; Proc. 30, 13; point out that the second isomeric azobenzene is probably an eutectic mixture of azobenzene with azoxybenzene.

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1. See Lecture recognition of ketones. [illegible] Chem. Soc. 80, 1446 (1958). Cortner and Cortner, Anal. Chemist, 29, 1291 (1957) Miller and Tourky, [illegible] Chem. Soc. 1, 3 9-111, Proc. 1, 101 point out that the alkaline isomerization mechanism is probably or similar mixture of mechanisms with monosubstituents.

has been obtained by this rearrangement.

Finally, the five dihydro- acids mentioned above have been converted into their dibromides and the dihydro- acids recovered from the latter. Fractionation of the recovered acids failed to give evidences of the presence of electromers.

It is admitted that the above work is open to the usual objections which are advanced to explain the non-existence of the required number of electromers, for example: (a) The electromers may have been present in such small quantities that they failed to be detected by the methods used; (b) Under the conditions of the experiment, only one of the many possible electromers is stable; etc. If, however, it is maintained that maleic and fumaric acids are electromers (and a score of other examples of geometrical isomerism might be chosen) then it must be admitted that many isomeric electromers are quite stable, and naphtho-electromers might be expected to be equally so.

Summary

1. The electron conpcetion of valence in its application to the explanation of cis-trans isomerism has been discussed.

2. A method of investigating this problem has been outlined as follows: (a) The necessity of working in a homologous series in which the speed of rearrangement is slow; (b) Exclusion of the possibility of geometrical isomerism; (c) Using the ionization constants rather than the melting points for identification of supposed electromers.

3. In the course of this work, several hundred mixtures of reduced naphthoic acids both in the alpha and the beta series have been examined and the structure of every compound obtained could be explained on the basis of the atomic linking theory.

1. The electron composition of matter in its application to the explanation of electrons inertia has been discussed.

2. Method of investigating this problem has been outlined as follows: (a) the possibility of proceed in a theoretical series by using the speed of measurement is slow; (b) solution of the possibility of geometrical interpretation; (c) using the interpolation solutions rather than the matching points for identification of suggested elementary.

3. In the course of this work, several important aspects of reduced magnetic scale both in the sphere and the inner series have been examined and the structure of every component obtained could be explained on the basis of the atomic linear chain.

PART III

THE CORRELATION OF IONIZATION AND STRUCTURE IN UNSATURATED ACIDS

III. TEAM

CRA, NITRATION, AND NITRAMINES, AND MEDIA CONTAMINATION BY EXPLOSIVES

III

THE CORRELATION OF IONIZATION AND STRUCTURE IN UNSATURATED ACIDS

Historical

The historical basis of this problem has been partly discussed in the general historical treatment given on pages six to nineteen. A more detailed review of the special part of the problem dealing with the correlation of ionization and structure in unsaturated acids will, however, be given here.

Soon after Wislicenus[1] had expanded and applied the hypothesis of Van't Hoff and Le Bel concerning the space arrangement of the four valences of the carbon atom, Ostwald[2] began the investigation of the compounds studied by Wislicenus from the standpoint of ionization, and attempted to assign the proper structure to individual isomers by means of the application of conductivity measurements. Adopting the formulae assigned by Wislicenus to crotonic and isocrotonic acids, Ostwald attempted by analogy to assign structures to other

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1. Kgl. Sächs. Ges. d. Wiss. 24, 1 (1887).
2. Z. physik. Chem. 3, 241 (1889).

[illegible]

The historical basis of this problem has been partially discussed in the general historical introduction given on pages six to nineteen. A more detailed review of the special part of the problem dealing with the correlation of inclusions and structure in weakened walls will, however, be given here.

Von Karman[1] has approached and solved the buckling problem of Van's Hall and the Dome considering the effect only of the load variations on the curved shell. Donnell[2] considers the interaction of the compressive buckling load in Warehouses in the elongation of connections, and multiplied by bending the proper authorities in industrial research to assess the application of qualitatively comprehensive. Analyzing the structural behavior of Warehouses in corporate and industrial areas, Donnell attempted to analyze in analogy structures in other

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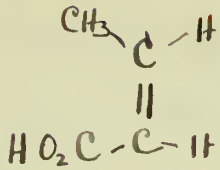
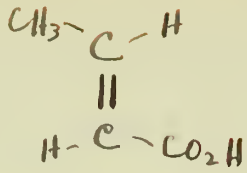
1. Th. v. Karman. Theo. u. Wiss. Ges. 1 (1907).
2. L. H. Donnell. Theo. u. Wiss. Ges. 1 (1907).

unsaturated acids.



Crotonic acid

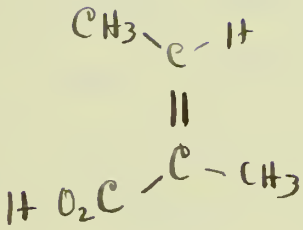
Ka^{25^o} 2.04×10^{-5}



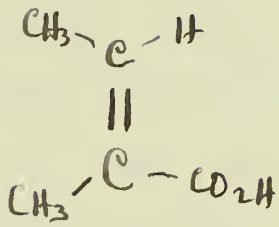
Isocrotonic acid

Ka^{25^o} 3.6×10^{-5}

One of the isomeric methyl crotonic acids (Angelic acid) has an ionization constant of $Ka^{25^o} = 5.0 \times 10^{-5}$ while for the other (Tiglic acid) $Ka^{25^o} = 9.6 \times 10^{-6}$. On the basis that the stronger acid is the one having a hydrogen in close proximity to the carboxyl group, Ostwald assigned the following formulae to the two isomers.



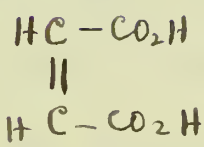
Tiglic acid



Angelic acid

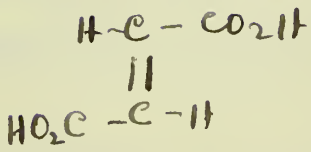
Similarly, other unsaturated acids were considered.

In the case of maleic and fumaric acids[1],



Maleic acid

$Ka^{25^o} = 1.17 \times 10^{-2}$



Fumaric acid

$Ka^{25^o} = 9.3 \times 10^{-4}$

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1. Ibid, pages 380-1.

[illegible]

Gamma ray	Isotopic mass
$E_{\gamma} = 1.0x \times 10^{-[illegible]}$	$m_{iso} = 0.[illegible] \times 10^{-[illegible]}$

One of the laboratory [illegible] experiments results (Angstrom mass) [illegible] an atomic [illegible] combined of $m_{A} = 0.0 \times 10^{-[illegible]}$ [illegible] for the [illegible] (Figures mass) $m_{F} = 1.[illegible] \times 10^{-[illegible]}$. On the basis that the [illegible] mass is the [illegible] of Europium [illegible] atoms [illegible] by the [illegible] group, Oswald assigned the [illegible] [illegible] to the [illegible] laboratory.

Tungsten mass	Angstrom mass

Similarly, [illegible] [illegible] mass [illegible] conversion was.

In the case of [illegible] the [illegible] masses,

Tungsten mass	Angstrom mass
$E_{\gamma} = 1.[illegible] \times 10^{-[illegible]}$	$m_{iso} = 1.[illegible] \times 10^{-[illegible]}$

1. Ibid, pages [illegible]-1.

the one having the two carboxyl groups on the same side of the plane of the double union was found to be the stronger acid, and this fact was therefore used to distinguish between analogous isomers.

It is thus apparent that the ionization constant measures the indirect (space) influence as well as the direct (chain) influence of a given substituent. This view which is so clearly and emphatically expressed by Ostwald has sometimes been forgotten by later investigators.

With the work of Fichter and Pfister[1], a distinct advance is made in this field, and for the first time the generalization is made that β,γ unsaturated acids possess a larger ionization constant than the α,β -isomers. Fichter and Pfister have also suggested that the double-union does not behave like a negative substituent, for in the latter case there is an uninterrupted decrease in ionization constant as the negative substituent is removed farther from the carboxyl group. Baeyer[2], after considering the ionization constants of the dihydronaphthoic acids, states that the decrease in the constant as we go from the Δ^2 to the Δ^1 position is rather unexpected but may be of value in explaining the "Mechanik der Ringsysteme."

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1. Ann. 334, 201 (1904); 348, 257 (1906).
2. Ann. 266, 175 (1891).

Fichter and Pfister have demonstrated that this behavior is a general one which holds for chain acids as well as for cyclic acids. The effect of geometrical isomerism due to the double union is not considered. A recent treatment of this subject has, however, been given by Roth and Stoermer.[1]

The explanation offered by Fichter and Pfister for the low ionization constants of α, β unsaturated acids is based upon the Theile Partial Valence Theory.[2] This view is also expressed by the writer on the basis of his conductivity measurements. According to Theile, α, β unsaturated acids contain a conjugated system of double unions. Thus we are here dealing with a more saturated and more stable compound than in the case of the β, γ unsaturated acid. We would expect the more perfectly neutralized compound to be also the most stable toward ionization. The Theile theory may therefore predict irregularities of this nature.

An altogether different explanation of the phenomenon discussed above has been offered by Michael[3] who believes that the double union <u>does behave like a negative substituent</u>. According to him, the apparent contradictions are due to the fact that other investigators have used <u>the wrong scale of</u>

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1. Ber. 46, 260 (1914?).
2. Ann. 306, 103 (1899).
3. J. Am. Chem. Soc. 34, 849 (1912).

influence. The complete explanation as given by Michael is:

> "An increase in the ionization constant takes place in passing from $\Delta^{\alpha,\beta}$ to $\Delta^{\beta,\gamma}$-acids, where, in the first group, the unsaturated carbons are in the fourth and fifth, while in the second, they are in the fifth and sixth positions, toward the carboxyl hydrogens."

The scale of influence referred to is i-2-5-6-4-3-7-9-10-11-8. It has already been discussed in the general historical treatment.

This problem has also been considered by Flürscheim[1] who has expressed his views as follows:

> "If we have, for example, an unsaturated atom substituting hydrogen in the α-position, the carbon atom will be more strongly bound by it; this leads to a reduction of the force with which the α atom binds the carboxyl-carbon atom, to a stronger linking between the latter and oxygen, and therefore to a weakening of the bond between oxygen and hydrogen."

Consequently the degree of ionization in this acid will be greater than in the unsubstituted one. An unsaturated atom substituting hydrogen in the β position would have exactly the opposite effect, and a weaker acid would result which agrees with observations. However, as we proceed to substitute the negative atom in the γ-position, we fail to get an increase over that found for the β-position; in fact, for the substitution of Cl, Br, OH, etc. we observe a gradual uninterrupted decrease in the place influence as the substituent is further

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1. J. Chem. Soc. 95, 718 (1909).

removed from the carboxyl group.[1] This is a serious objection to the theory.

Flürscheim believes that the ionization constants of the unsaturated aliphatic acids lend support to his views. He states:

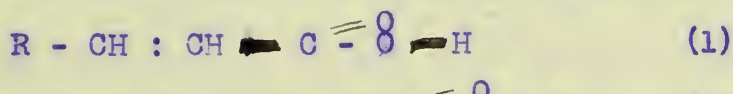
> " α, β and γ, δ -unsaturated acids are weaker than β, γ-unsaturated acids, notwithstanding that in the α, β -acid the negative double linking is nearest the carboxyl group."

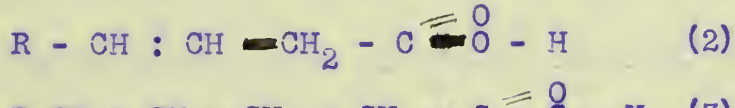
The support for this statement is given in the following table:

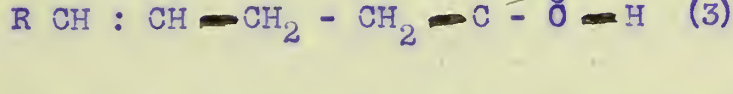
Table 9

	100 K		100 K
Valeric acid	0.00161	n-Hexanoic acid	0.00146
α,β-Pentenoic acid	0.00148	$\alpha\beta$ Hexanoic "	0.00189
$\beta\gamma$-Pentenoic "	0.00335	$\beta\gamma$ Hexanoic "	0.00264
$\gamma\delta$ Pentenoic "	0.00209	$\gamma\delta$ Hexanoic "	0.00174
		$\delta\epsilon$ Hexanoic "	0.00191

Graphically, this effect is represented thus:







In the above series, acid (2) is therefore predicted as being stronger than either (1) or (3) which is in agreement with observation.

For the Δ^1, Δ^2 and Δ^3 unsaturated acids, this prediction agrees with that suggested by the Theile theory. The two views would, however, differ in their prediction of the ,

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1. J. Am. Chem. Soc. 33, 1174-75 (1911).

Δ^4, Δ^5, etc. double unions. The Flürscheim view in the case of the unsaturated acids is favored by the single fact that Δ^4 hexenoic acid has a greater ionization constant than Δ^3-hexenoic acid. This argument is shown to be weak if we ask the following question: Which one of the two possible Δ^3-hexenoic acids was measured, the cis- or the trans- form, or was it an equilibrium mixture? Flürscheim has neglected the possibilities of cis-trans isomerism. He has disregarded the data presented by Ostwald, who has so definitely shown that space isomerism is reflected in the ionization constant.

We may, however, test out the Flürscheim rule by considering a Δ^3 unsaturated acid which has the double union linked to the last carbon atom as illustrated below, thus giving a case parallel with that of Δ^4-hexanoic acid, since in both cases only one space form is possible. The measurements on Δ^3-pentenoic acid have been repeated in this laboratory by Hollman[1] and the previous measurements confirmed.

$$Ka^{25^\circ} = 2.09 \times 10^{-5\#}$$
$$Ka^{25^\circ} = 1.88 \times 10^{-5}$$

If we take into consideration the fact that valeric acid is a stronger acid than caproic, we still find that the place influence for a double union in the Δ^3-position is at least as

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1. B. S. Thesis. Univ. of Illinois. 1912.
Corrected values.

large as that for the Δ^4.

A relation between the rearrangements of unsaturated acids and their ionization constants has recently been advanced by Derick[1], who has shown that intramolecular rearrangements of the non-reversible type take place in the direction to decrease the free energy of ionization.

Theoretical Part

A preliminary study of the ionization constants of unsaturated acids reveals the fact that no quantitative correlation, sufficiently accurate to be of value for the prediction of the structures of unknown compounds, appears to exist between the ionization constants and the atomic linking structure of these acids. The reason for this may be found partly in the fact that the experimental data may be somewhat inaccurate, but more probably is to be sought in the fact that we have neglected the possibility of cis-trans isomerism. In some cases, we are comparing the ionization constant of a cis- acid with that obtained from an acid which is really a trans isomer; in many cases , especially when the unsaturation is farther removed than the $\alpha\beta$-position from the carboxyl group, we may be measuring a mixture of isomers; and finally, we are not justified in comparing the unsaturated with the corresponding saturated acids since in the former the positions of certain groups in

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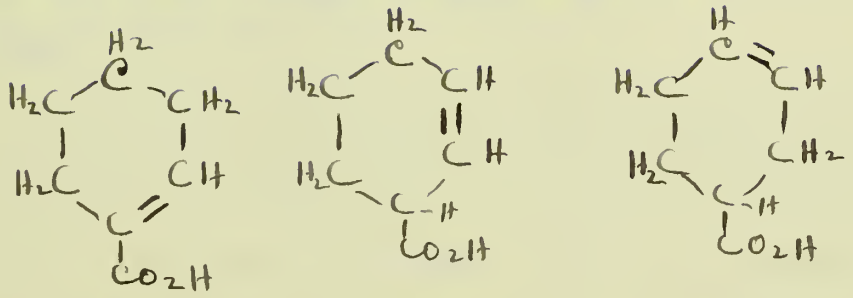
1. J. Am. Chem. Soc. 32, 1333 (1910).

space are fixed, whereas in the saturated acid, free rotation between the carbon atoms is possible, and this relation would vary for each pair of acids measured.

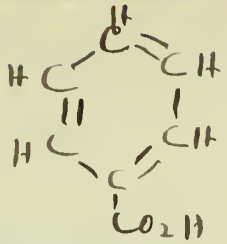
Because of these complicating influences, the present investigation deals with acids in which cis-trans isomerism due to the double union will not interfere. To make this possible, acids having the unsaturation in a ring of carbon atoms have been chosen. In determining the effect of a given double-union the ionization constant may therefore be referred to the hydrogenated acid which has its atoms in approximately the same space arrangement. The present work has been in the naphthalene series partly for this reason and also because of the fact that in this series the speed of reaction is slow and consequently the acids may be prepared in a purer condition. As has already been pointed out, dangers due to oxidation and rearrangement are also less liable to take place.

The use of ionization for the prediction of structure may be illustrated by the following typical example. If we determine quantitatively the separate effects of the double unions in the three tetrahydrobenzoic acids

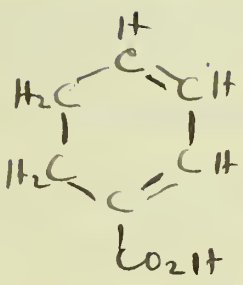


I II III

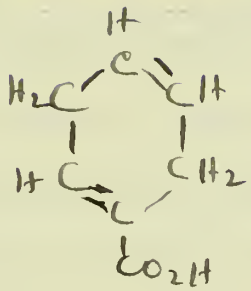
we could determine whether benzoic acid has the structure



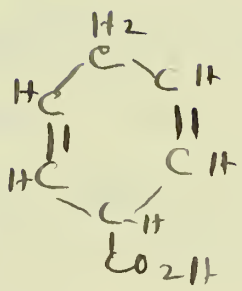
since the latter formula contains the three double unions (Δ^1, Δ^2 and Δ^3) represented in the tetrahydro- benzoic acids above. Before proving this, however, it would first be necessary to determine whether the influences of double unions are really additive. This would be accomplished by measuring the ionization constants of some of the dihydrobenzoic acids



IV



V



VI

If the effect of the double unions is additive, IV and V (above) should have the same ionization constants, and we should be able to predict the ionization constants of IV, V and VI, knowing the values of I, II and III together with the ionization constant of hexahydrobenzoic acid.

The present investigation has not gone as far as this; but it may throw some light upon the question of whether the above method of attack is feasible. It has attempted to determine

[illegible]

[illegible]

IV V VI

[illegible]

[illegible]

whether the place influence of a double union in a given position in a carbon ring is constant, and whether the additive relation holds.

Experimental Part

Preparation and Purification of the Acids Measured

The methods used for the preparation and purification of the acids studied in this work have been described in detail in Part I. For the preparation of the dihydro-β-naphthoic acids and the tetrahydronaphthoic acids, similar precautions were used as those described. Final purification always took place in well-steamed flasks of Jena glass. Usually the centrifuge was used in preference to the suction pump for the separation of the mother liquor from the crystals. The alcohol and acetone solutions used for the final purifications were of such purity that when added to conductivity water they did not appreciably change its conductance. In general, two samples of each acid were used in the measurements, one of which had received its final crystallizations from aqueous solvents and the other from organic solvents. For this purpose, low-boiling ligroin was used in most cases, the latter having been redistilled and its purity tested by shaking it with conductivity water of known purity and then again measuring the conductivity.

[illegible]

[illegible]

[illegible]

[illegible]

The Conductivity Water

The water was distilled from an alkaline permanganate solution, discarding the first portions containing ammonia. It was collected hot, in 4-liter resistance-glass flasks which had been used for this purpose during a number of years. It was easily possible to obtain water having a specific conductance of 0.5 to 0.8 x 10^{-6} reciprocal ohms.

Apparatus

The thermostat used, consisting of a 4-liter Dewar bulb fitted with a stirrer, cooling coil and electrical heating coil, was similar to that used by the U.S. Geological Survey[1] in its accurate temperature control work.

The Kohlrausch method[2] was used for the measurement of conductivity. Both the bridge which was of the drum type manufactured by the Leeds and Northrup Co. as well as the Decadé resistance boxes used have been previously described and their calibrations recorded.[3] The main changes made from the method previously in use in this laboratory consists in the use of the Paul# telephone manufactured by Robert W. Paul, of New

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1. This fact was pointed out by Dr. A. Day, who inspected the apparatus while on his recent visit to the University.
2. Kohlrausch and Holborn. Leitvermögen der Elektrolyte, Leipzig, 1898.
3. See Prasil, B.S. Thesis, Univ. of Illinois. 1914.

The value of this telephone in conductivity has been proven by the valuable investigation of E. W. Washburn and his co-workers in the Physical Division of these Laboratories.

Southgate, London and tuned to 1000 cycles and possessing a resistance of 150 ohms. With the use of the latter, extremely satisfactory end-points could be obtained. A modification in the use of conductivity cells was also applied.

The Conductivity Cells

These were of the pipette type. The usual salt-acid cell with platinized electrodes was, however, not used since it was found possible to obtain equally accurate and often better end-points by using cells with unplatinized electrodes, provided several cells with varying capacities were used during the course of the dilutions. For concentrations above .0005 N a cell with a constant of 0.1031 was used, while thru concentrations of .0005 N to .0001 N a cell with a constant of 0.01950 (water cell) was used. By doing this, the catalytic oxidation of the unsaturated acids measured was prevented. The cell constants were determined by several comparisons with the salt-acid cell, the constant of the latter having been obtained with a standard potassium chloride solution prepared as directed by Kohlrausch and Holborn.[1]

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1. When preparing .02 N and .01 N KCl solutions, it should be noted that an error is made in the directions (page 77) given by these authors, the quantities of KCl used (1.486 gm. and 0.7430 gm.) being incorrect.

Preparation of Solutions

The usual volumetric method for the determination of the normality of the solutions used was not followed, because of the very slight solubility of most of the acids measured. Due to the latter, the solution titrated would be too dilute to give satisfactory end-points. Instead, the sample of acid was weighed and water added to bring the solution up to the desired standard weight. The original solution as well as the dilutions were made up by weight, and for this reason a table of specific gravities is given in case it is thought desirable to change the concentrations into terms of volume normal. In each case, the first solution was made up in a flask in which conductivity water was collected initially, thus rendering a transfer of the water for the first concentration unnecessary.

In order to weigh the sample with sufficient accuracy, at least 0.1000 grams of material and preferably a larger weight was used. For this reason, it was often desirable to prepare as much as two liters of the first solution in the case of the less soluble acids.

Because of the difficulty of dissolving the acids, it was often found necessary to warm the solutions slightly on the electrical hot-plate. In some cases, the weighed sample was added directly to the conductivity water before the latter had cooled to room temperature, first, however, withdrawing a sample

for measurement. In doing this, attention is directed to the danger of error brought about in bringing the weighing flask up to the mouth of the bottle containing the warm water. If the material is not hygroscopic, it is better to weigh it out on a weighed, well-steamed 2.5 cm. watch glass, adding the latter together with material to be measured; making an allowance, however, for the weight of the glass in diluting to the proper weight.

An attempt was initially made to weigh out the material into a steamed flask, and to dissolve it by the addition of 1 cc. of pure ethyl alcohol or acetone, quickly reprecipitating it in a finely divided form, in which case it will dissolve readily, by the addition of the conductivity water. It was found, however, that a concentration of 0.1% of alcohol changed the conductivity of the solution by about 0.4% and hence this method could not be used. This result is in agreement with observations of others.[1]

All the conductivity measurements have been made at a temperature of 25° C ± 0.01°.

Specific Gravities of the Solutions

If it is desired to change the concentrations given in the following tables into terms of volume normal instead of

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1. Jones, J. Am. Chem. Soc. 36, 2243 (1914).

weight normal, the following specific gravities may be used:

Table 10

Concentration	Sp. Gr. $d^{25^o}_{25^o}$
0.004 N	1.00014
0.002 N	1.00008
0.001 N	1.00004
0.0005 N	1.00002
0.00025 N	1.00000
0.000125 N	1.00000

The acid used for the above determinations was Δ^2-dihydronaphthoic acid-1. The results will serve for the densities of corresponding solutions of the other naphthoic acids, as was found by actual measurement.

Ionization Constants of β-naphthoic Acid and of the Reduced α and β-naphoic Acids

In the calculation of the ionization constants as given in the following tables, the value for the conductivity at infinite dilution (Λ_o) was calculated from the Ostwald rule[1]. Before presenting final results for the constant, however, these values will be determined by the salt method. A few of the ionization constants given below are also to be regarded as preliminary values and will be redetermined. In the tables given,

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1. See Lunden's "Affinitatsmessungen an Schwachen Säuren und Basen." Page 9.
Sammlung Chemischer und Chem. tech. Vorträge, vol. 14, 9 (1909).

C = concentration of the acid

Λ = equivalent conductance at 25° at the concentration C uncorrected for the conductivity of the water used

K = ionization constant calculated according to the equation #

$$K = \frac{c\lambda^2}{\lambda_0(\lambda_0-\lambda)}.$$

β-naphthoic Acid

This acid has been measured by both Bader[1] and by Bethmann[2]. The values for Ka^{25° found are as follows:

$Ka^{25^\circ} = 5.23 \times 10^{-5}$ Bader

$Ka^{25^\circ} = 6.78 \times 10^{-5}$ Bethmann

Each one of the above values is, however, based upon measurements at only one dilution. The reason for this is the extermely slight solubility of the acid (less than one part in 30,000 parts water).

Because of the disagreement in the values given above, the measurements on this acid have been repeated and an attempt has been made to measure it at varying concentrations.

#The values for λ are taken from two or more check solution.

1. Z. physik. Chem. 6, 311 (1890).
2. Ibid, 5, 399 (1890).

Table 11

β-naphthoic acid m. pt. 185.5°

Water used = 0.7×10^{-6}

C	λ	$Ka^{25°}$
.0003 N	142.7	6.92×10^{-5}
.0002 N	165.3	6.85×10^{-5}
.0001 N	206.8	6.67×10^{-5}

These results agree with the observation of Bethmann whose results have not been corrected for the error in the mobilities of the various ions involved.

Table 12

Δ^1-dihydronaphthoic acid-2

m. pt. 118.5° Water used 0.7×10^{-6}

C	λ	$Ka^{25°}$
.0005 N	80.57	2.92×10^{-5}
.00025 N	108.3	2.91×10^{-5}
.000125 N	142.56	2.90×10^{-5}

The ionization constant of the new isomeric dihydro- acid described in Part I, thus differs only slightly from the value uncorrected given by Bader for the other isomer having a double union in the Δ^1-position in respect to the carboxyl group; i.e. the so-called Δ^2-dihydronaphthoic acid-2. A redetermination of the constant of the latter has given results somewhat lower

than expected from the ionization constant of the tetrahydro-acid and for this reason the measurements will be repeated.

Table 13

Δ^2-dihydronaphthoic acid-2

m. pt. 161° Water used = 0.65×10^{-6}

C	λ	$Ka^{25°}$
.0005 N	76.4	2.59×10^{-5}
.00025 N	102.3	2.54×10^{-5}
.000125 N	134.4	2.49×10^{-5}

Table 14

Δ^3-dihydronaphthoic acid-2

m. pt. 101.2° Water used = 0.55×10^{-6}

C	λ	$Ka^{25°}$
.002 N	58.86	5.81×10^{-5}
.001 N	80.19	5.78×10^{-5}
.0005	107.43	5.72×10^{-5}
.00025	141.2	5.65×10^{-5}
.000125	180.7	5.56×10^{-5}

Table 15

ac- Tetrahydronaphthoic acid-2

m. pt. 96° Water used 0.6×10^{-6}

C	λ	$Ka^{25°}$
.003 N	32.60	2.48×10^{-5}
.002	39.66	2.49×10^{-5}
.001 N	54.21	2.44×10^{-5}
.0005 N	73.94	2.41×10^{-5}

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Table 16

Δ^1-dihydronaphthoic acid-1

m. pt. 121.5° Water used 0.65×10^{-6}

C	λ	$Ka^{25°}$
.001 N	92.19	7.96×10^{-5}
.0005 N	122.66	7.90×10^{-5}
.00025 N	159.47	7.81×10^{-5}
.000125 N	200.5	7.62×10^{-5}

Table 17

Δ^2-dihydronaphthoic acid-1

m. pt. 86° Water used 0.84×10^{-6}

C	λ	$Ka^{25°}$
.004 N	59.02	11.69×10^{-5}
.002 N	80.3	11.60×10^{-5}
.001 N	107.8	11.52×10^{-5}
.0005 N	141.85	11.43×10^{-5}
.00025 N	181.66	11.3×10^{-5}
.000125 N	224.62	11.1×10^{-5}

Δ^2-dihydronaphthoic acid 1 is rapidly decomposed if its solution is measured with platinized electrodes. The decomposition is probably an oxidation, which is followed by the loss of carbon-dioxide and the formation of naphthalene. The above values were, of course, obtained with the unplatinized electrodes. A similar difficulty is reported by Ostwald[1] in the measurement of formic acid.

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1. Z. physik. Chem. 3, 174 (1889).

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Table 18

ac-Tetrahydronaphthoic acid-1

m. pt. 85° Water used 0.8×10^{-6}

C	λ	$Ka^{25°}$
.002 N	52.3	4.49×10^{-5}
.001 N	71.4	4.45×10^{-5}
.0005 N	96.06	4.39×10^{-5}
.00025 N	127.7	4.37×10^{-5}
.000125 N	165.3	4.31×10^{-5}

Discussion of Results

In general, it may be said that the ionization constants reported by Bethmann[1] have been verified, whereas those by Bader[1] have not received as complete a substantiation. Altho the values reported by the writer are not considered as final in a number of cases, the following calculations serve to show that they are more accurate even in their present form than those given in the literature.

In a recent article, Derick[2] has advanced a method for the detection of errors in conductance data. This sensitive criterion of the precision and of constant errors in conductance data of weak electrolytes is the "calculated λ_o". It is obtained from the two equations

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1. Loc. cit.
2. J. Am. Chem. Soc. 36, 2268 (1914).

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$$K = \frac{C\lambda^2}{\lambda_0(\lambda_0 - \lambda)}.$$

and $$K = \frac{C_1\lambda_1^2}{\lambda_0(\lambda_0 - \lambda_1)}$$

by equating them and solving for λ_0 (i.e. the conductance at infinite dilution).

The result is as follows:

$$\lambda_0 = \frac{\lambda\lambda_1(C\lambda - C_1\lambda_1)}{C\lambda^2 - C_1\lambda_1^2}$$

, in which λ and λ_1 represent the molar conductances of a given electrolyte at the two concentrations C and C_1 respectively.

Applying this criterion to Bader's data for ac-tetrahydronaphthoic acid-2, we obtain the values for λ_0 given below.

Bader's data for ac-tetrahydronaphthoic acid-2

	C	λ
(1)	.004859	23.86
(2)	.002429	33.73
(3)	.001214	47.13
(4)	.000607	65.14

The calculated λ_0's are found to be as follows:

Combination used	found
1 and 2	1013
1 and 3	947
1 and 4	623
2 and 3	587
2 and 4	324
3 and 4	449

The theoretical value is about 375.

Bader's data for Δ^3-dihydronaphthoic acid-2

C	
.004411 N	35.8
.002206	49.86
.001103	69.1

The calculated values for λ_0 are here found to be 505, 522 and 535 respectively, using the combinations suggested above.

Using the writer's data for the same acid, as given in Table 14, page 93, the values obtained for λ_0 are:

Combinations used	λ_0
1 and 2	356
1 and 3	349
1 and 4	350
1 and 5	355
2 and 3	346
2 and 4	352
2 and 5	355
3 and 4	355
3 and 5	357

Similarly, the values for λ_0 calculated from the data given for β-naphthoic acid (Table 11, page 92) are as follows:

Combinations used	found
1 and 2	357
1 and 3	356
2 and 3	356

Conclusions

The following ratios show that the value for a Δ^2 double bond in the cyclic acids is fairly constant whereas in the unsaturated aliphatic acids no such regularity was found.

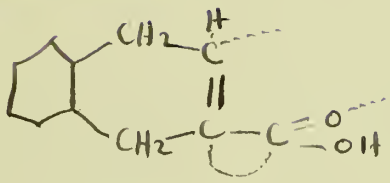
$$\frac{K \text{ for } \Delta^{3\#} \text{ dihydronaphthoic acid-2}}{K \text{ for ac-tetrahydronaphthoic acid-2}} = \frac{5.74}{2.47} = 2.33$$

$$\frac{K \text{ for } \Delta^{2}\text{-dihydronaphthoic acid-1}}{K \text{ for ac-tetrahydronaphthoic acid-1}} = \frac{11.6}{4.43} = 2.61$$

$$\frac{K \text{ for } \Delta^{2}\text{-tetrahydrobenzoic acid}}{K \text{ for hexahydrobenzoic acid}} = \frac{3.05}{1.28} = 2.38$$

This regularity is not found in the case of the Δ^{1} double unions, and the explanation for the deviation is sought in the fact that we are here dealing with acids in which the degree of conjugation of the Δ^{1}-double union with the carbonyl double union varies.

Using the Theile Partial Valence Theory and applying it to two acids



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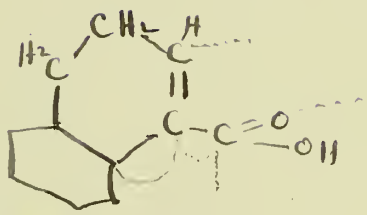

II

we would predict that as the unsaturated phenyl ring in acid I is brought into conjugation with the partial valence on the α carbon (as is the case in structure II) that we would obtain a stronger acid. This would be predicted because according to the Theile view conjugation of the Δ^{1} double union has given a

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The double union is here in the Δ^{2} position in respect to the carboxyl group, but since Meyer and Jacobson have adopted Baeyer's nomenclature, the writer has also done so.

weaker acid than initially expected and the removal of this conjugation partly reverses the effect. A quantitative measure of the degree of conjugation is therefore available if this is found to hold generally.

The ionization constant of Δ^2-dihydronaphthoic acid-2 is only slightly larger than that of the tetrahydro- acid, whereas in the case of Δ^1-dihydronaphthoic acid-1 (structure II) we find an acid approaching more nearly the value for the Δ^2 double union:

$$\frac{K\ \Delta^1\text{-dihydronaphthoic acid-1}}{K\ \text{ac-tetrahydronaphthoic acid}} = \frac{7.90}{4.43} = 1.78$$

Summary of Parts I, II and III

1. The missing isomeric dihydro-β-naphthoic acid has been prepared by rearrangement of both Δ^3-dihydronaphthoic acid-2 and Δ^2-dihydronaphthoic acid-2 and its identity as a pure chemical individual has been established.

2. The structures of the three isomeric dihydro- acids have been demonstrated thru the reactions of the corresponding dibromides.

3. The structure of Δ^1-dihydronaphthoic acid has been conclusively established by means of oxidation reactions.

4. The electron conception of valence in its application to the explanation of cis-trans isomerism has been discussed.

5. A method of investigating this problem has been outlined as follows: (a) The necessity of working in a homologous series in which the speed of rearrangement is slow; (b) Exclusion of the possibility of geometrical isomerism; (c) Using the ionization constants rather than the melting points for identification of supposed electromers.

6. In the course of this work, several hundred mixtures of reduced naphthoic acids both in the alpha and the beta series have been examined and the structure of every compound

obtained could be explained on the basis of the atomic linking theory.

7. The ionization constants of eight monocarboxy- naphthalene derivatives have been measured.

8. The place influence for a double union in the Δ^2 position in respect to the carboxyl group has been shown to be a constant for the cyclic acids. The dangers of drawing conclusions from the ionization constants of unsaturated aliphatic acids where cis-trans isomerism due to the double union is possible, have been emphasized.

9. The place influence for a Δ^1 double union has been shown to vary with the degree of conjugation and it is suggested that a quantitative interpretation of Theile's partial valence theory may be developed from this standpoint which will be generally applicable.

Vita

The writer of this dissertation was born in Highland, Illinois, Dec. 6, 1888 and received his elementary and high school education in the schools of this city, graduating in 1906. He entered the University of Illinois in 1907 and received the degree of B.S. in Chemistry in 1911 and the M.S. degree in 1913. During the years 1911-15 he has been an assistant in the Chemistry Department of the University. He has also served as assistant during the summer sessions of 1913 and 1914. His publications consist of two papers, "A Study of Cobaltinitrites and Their Application to Analytical Chemistry", by Laurie L. Burgess and Oliver Kamm, J. Am. Chem. Soc. 34, 652-59 (1912); and "A Study of the Mechanism of the Grignard Reaction" by Lambert Thorp and Oliver Kamm, J. Am. Chem. Soc. 36, 1022-28 (1914). He is a member of the American Chemical Society, Sigma Xi and Phi Lambda Upsilon.